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Photocatalytic disinfection of natural well water contaminated by *Fusarium solani* using TiO_2 slurry in solar CPC photo-reactors

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ABSTRACT

Phytopathogenic infection of food crops with fungi such as *Fusarium* spp. is a major problem faced by the farming industry and it has a major economic impact through the reduction in crop yields and through the need to use chemical pesticides to control the problem. As fungi are resistant to many disinfecting agents, which may also be phytotoxic or create environmental problems, more and more effort is being invested in the development of new control techniques for phytopathogenic fungi. It has recently been demonstrated on a small scale that the *Fusarium*, and within it, *Fusarium solani,* a plant and human pathogen, is susceptible to solar photocatalytic disinfection with TiO_2 in distilled water.We report on disinfection of water contaminated by *F. solani* spores using a solar bottle reactor and a 14-L CPC solar photoreactor with distilled and also with natural well water. It was possible to reach high disinfection yields with different TiO_2 concentrations (from 10 to 500 mg L^{-1}) and state flow conditions (20 L/min), at these volumes, not only in distilled, but also in natural well water. We also give the inactivation rate constant for the first stage of photocatalysis under the various experimental conditions, for selection of the best parameters for disinfecting water with phytopathogenic fungi in a future pilot treatment plant.

1. Introduction

The heavy demand for water in agriculture makes sustainable access more and more important. Water from many sources used or reused in agriculture is contaminated by phytopathogens and has to be disinfected. According to the Food and Agriculture Organization of the United Nations (FAO), agriculture consumes 70% of fresh water used worldwide. In developing countries, this increases to over 95% of the available fresh water. The average water used for crops is around 1000–3000 m^3 per ton of cereal harvested, or in other words, 1–3 tons of water are used to grow 1 kg of cereal. Bearing in mind that the daily drinking-water requirement per person is only 2–4 L, it is often forgotten that it still takes 2000–5000 L of water to produce a person's daily food requirement [1,2].

80% of land cultivated worldwide is today still exclusively rainfed, and supplies over 60% of the world's food. Irrigation could triple or quadruple this production. However, the FAO does predict a sharp increase in irrigation replacing rainfed agriculture [2]. Stored rainwater or surface water used for irrigation accumulates phytopathogens as phytopathogenic bacteria and fungi can be found almost everywhere. The plant and human pathogen *Fusarium solani* has been reported as found almost everywhere, and in 2001, even in hospital water distribution systems [3].

The spores of phytopathogenic fungi are especially resistant to many environmental factors [4], easily spreading in traditional plantations and particularly in soilless cultures where diseases are often waterborne and reach the plants in the nutrient solution [5,6]. Our target for disinfection, the filamentous fungi *F. solani*, for example, has been reported in soils throughout the world [7,8] and even in hospital water distribution systems [3].

Solar photocatalytic disinfection with TiO_2 make use of the reactive hydroxyl radicals produced by the semiconductor surface in contact with the water under irradiation by sunlight at $\lambda \leq 400$ nm. Hydroxyl radical generation takes place in various reaction steps and is accompanied by coreactions depending on the catalyst surface and the molecules in the water, as fully described elsewhere [9]. Due to the strong reactivity of the radicals generated, especially the $^{\bullet}OH$ radicals, TiO_2 has already been used in many different applications for hazardous chemicals in water [9–11]. Disinfection with TiO_2 was first reported in the eighties for the Gram-positive bacteria *Lactobacillus acidophilus*, the Gram-negative bacteria *E. coli*, and the yeast *S. cerevisiae* [12,13].

Very recently, the disinfection of water containing the oocysts of the important, very chlorine-resistant pathogen, *C. parvum* [14], and spores of several species of the fungus genus *Fusarium* have been reported at laboratory scale and in distilled water [16,17]. Although the interaction of the catalyst and the cell wall was

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neglected in the beginning [12,13], recent literature explains the disinfection process by lipid peroxidation of the cell wall followed by lesions on microbial cell walls and leakage of cell content into the media [24,25]. Probably, in most of these cases, the TiO_2 sticks to the microbial cell wall where the radicals generated produce these lesions, as observed in disinfection of *Fusarium* spores with TiO_2 slurry [15]. This disinfection mechanism is only applicable to slurry systems as in immobilized systems particles cannot be absorbed onto pathogen surface.

Our previous work demonstrated the susceptibility of *F. equiseti*, *F. oxysporum*, *F. anthophilum*, *F. verticillioides*, and *F. solani* to disinfection with TiO_2 slurry in distilled water in 250-mL flasks under solar irradiation [15]. However, the process has to be upscaled for any application, especially water treatment for reuse and irrigation in agriculture. Unfortunately, the upscaling process is always complicated by different flow regimes, irradiation conditions, oxygen supply, etc. Therefore, to date, although some studies have worked on photocatalytic disinfection of water with phytopathogenic fungi using solar CPC reactors at pilot plant scale [17–19,22], there are none on applications for water reuse for irrigation. *F. solani* was chosen for this study based on our previous experience, because of its resistance to disinfection media and because of its ubiquitousness.

This paper reports on the disinfection of water contaminated with *F. solani* spores in a CPC reactor for solar photocatalytic disinfection. The efficiency of solar photocatalysis was experimentally demonstrated in 14 L of distilled and natural well water in 5 h of treatment time. The effects of catalyst concentration, adjusted to the system used, type of water, and flow rate are analyzed.

2. Materials and methods

2.1. Fungal strain, cultivation and enumeration

The wild strain of *F. solani* was acquired from soil cultures in Almería (southern Spain). Fungal colonies were transferred to agar sporulation media containing potassium chloride and kept at 25 °C for 15 days to produce microconidia, macroconidia and chlamydospores. The same strain and sporulation method had been used previously [15,19]. The spores were washed with sterile water from the mycelia and agar. The resulting suspension was centrifuged at 2000 × *g* for 10 min and washed three times with sterilized, distilled water. The spore concentration was found with a counting chamber (Neuenbauer improved). Then the spore suspension was diluted and poured into the reactors. Depending on fungal spore production on the agar plates, the initial spore concentration of the experiment varied from 1 day to the other between 0.3 and 1×10^3 CFU/mL.

The reduction in fungal concentration in the photoreactors exposed to sunlight was conducted through the standard plate count method after a series of 10-fold dilutions (10 and 100-fold). Volumes of 50–500 μL from the samples were plated out on acidified malt agar (Sigma–Aldrich, USA). Where fewer than 10 colonies per plate were observed, 500 μl of the sample was replated until a detection limit of 2 CFU/mL could be reached. 10

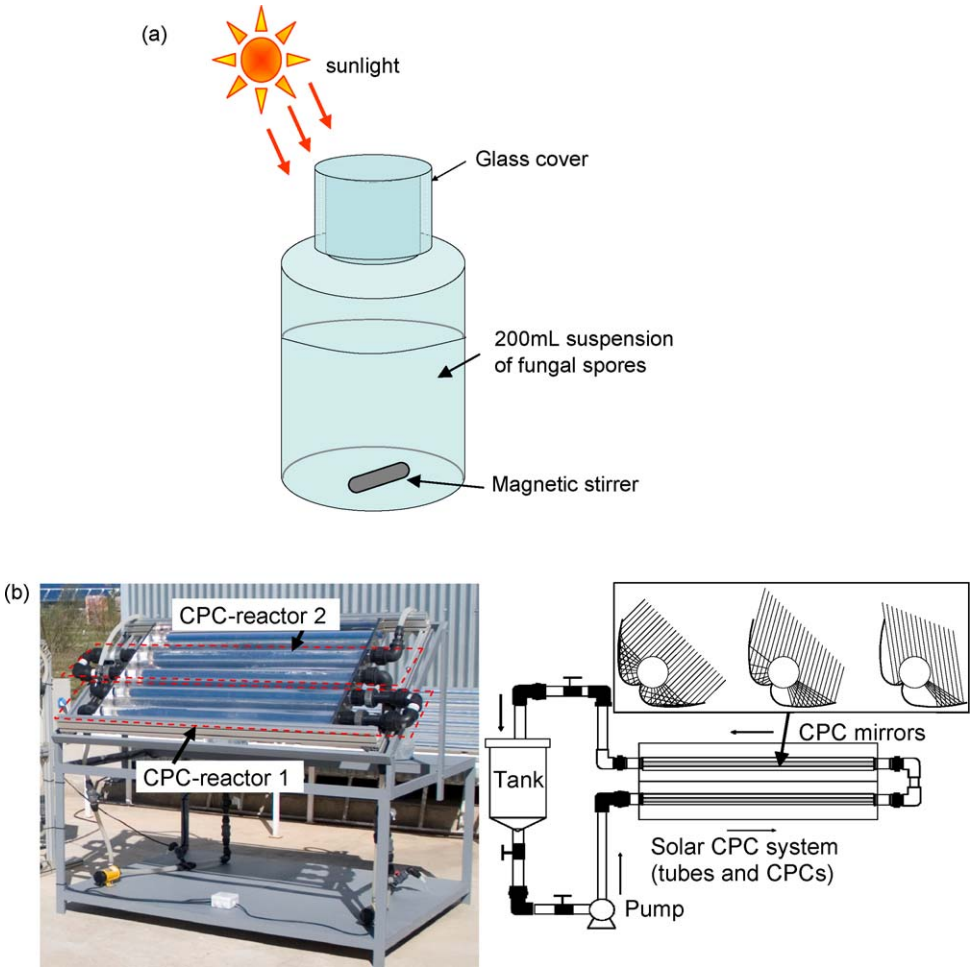

Fig. 1. Drawing of 250-mL glass bottle reactor (a). Photos of 2 solar CPC phototocatalytic reactors, and diagram of one of the two identical solar CPC systems (b).

and 100-fold dilutions of the original sample. Measurements were made in triplicate, with three sample inoculations on three plates. Fungal colonies were counted after 2 days of incubation at 28 °C in the dark. Measurements were analyzed by one-way ANOVA with $P < 0.05$, Confidence > 95% (Origin v7.0300, OriginLab Corp., Northampton, USA).

2.2. Solar bottle reactor

The experiments were performed in 250-mL glass reactor bottles (DURAN, Schott, Germany) with 200 mL total volume of treated water. Glass covers (Schott) were used instead of plastic lids to allow the solar radiation to enter the bottle reactor from all directions. The bottles were stirred with magnetic stirrers at 100 rpm during the experiment (Fig. 1a). Bottle experiments were done as previously as proof-of-principle experiments. All experiments were performed in triplicate at the PSA. Solar photocatalytic and solar-only disinfection tests were carried out simultaneously. Control samples were prepared in two different bottles, one with and another without TiO_2, which were stored under the same conditions as the disinfection test bottles, but in the dark. The fungal spores were added to the total 200-mL volume of water and left for 15 min in the dark (adaptation and homogenization time). Then the TiO_2 slurry catalyst was added and the bottle reactors were exposed to natural solar irradiation.

2.3. Solar CPC photoreactors

All experiments were performed under natural solar radiation at the Plataforma Solar de Almería, Spain, located at 37°84′ N and 2°34′ W. The solar CPC reactors were designed and built by AO SOL (Lisbon, Portugal). The system is described elsewhere [19,22]. The photoreactor volume is 14 L, the illuminated volume is 4.7 L, and the irradiated collector surface is 0.4 m^2. The fungal suspension was left recirculating in the reactor for 15 min in the dark (adaptation and homogenization time). Then the first sample was taken and the reactor was exposed to solar irradiation. All samples were taken in 50 mL tubes. The first sample was kept in the dark at room temperature and analyzed again at the end of the experiment to determine the decrease in fungal concentration in the dark.

The experimental setup allowed two experiments to be carried out simultaneously in two identical solar CPC reactors (Fig. 1b). Table 1 shows the general characteristics of the two solar systems used for the experiment. The experiments were performed simultaneously to compare the action of the photocatalyst with the action of sunlight only. All experiments were repeated three times. Disinfection conditions can vary significantly on different days due to changes in irradiation and temperatures. All experiments were for 5 h exposure to solar radiation and started between 11:00 and 11:30 a.m. local time on completely sunny days. In spite of the variability of the solar UVA irradiance during the experiments, it was similar every day, since all experiments were done in the same season and at the same time of day. Therefore, the results are presented as the average of the three replicates. The water temperature in the reactor was monitored during all the experiments and was always below 35 °C. Fungal viability is unaffected by these temperatures [26,27].

Table 1
Experimental conditions of solar experiments.

	Glass bottle reactor	CPC reactor
Total treatment volume	0.2 L	14 L
Irradiated volume	0.2 L	4.5 L
CPC mirror	–	2 CPCs
Irradiated surface	0.0095 m^2	0.4 m^2
Agitation	Magnetic	Centrifugal pump
Velocity/Flow rate	100 r.p.m.	20 L/min
TiO_2–P25	0–100 mg/L	0–500 mg/L
Initial concentration of fungal spores	$(1.0–2.2) \times 10^3$ CFU/mL	
Irradiation	Natural solar light in clear days	
Solar-UVA irradiance	25–37 W/m^2 (averaged during exposure)	

2.4. Photocatalyst

The catalyst was P25 TiO_2 (Degussa, Germany) applied as slurry. The optimal catalyst concentration for this kind of experimental setup was estimated using the following principles: the solar UV spectrum radiates on a 300–400 nm wavelength. Taking the relationship between light extinction in the UV range (I/I_0, I_0: incoming intensity, I: light intensity attenuated by the suspension), catalyst concentration ([TiO_2], mg/L), optical path length (L, cm) and TiO_2 extinction coefficient averaged in the UV-range (β^* = 51305 cm^2/g), the concentration of the catalyst for which light loss is minimal (i.e. ≤1%) may be calculated with the following equation [28]:

$$A = -\log\left(\frac{I}{I_0}\right) = L_{99} \cdot [\mathrm{TiO_2}] \cdot \beta^* \quad (1)$$

This concentration was estimated to be 35 mg/L for the bottle reactor and 83 mg/L for the CPC reactor, when total light extinction is 99% of the incoming solar intensity. For this estimate, we took a bottle reactor *internal diameter* of (11 cm) = L_{99}; and CPC reactor *inner radius of* (2.32 cm) = L_{99}, since with the CPC mirrors, radiation comes from all directions.

2.5. UV solar radiation measurement and assessment

Results were evaluated as the difference in inactivation over time between solar photocatalytic and dark control samples during simultaneous experiments. To take the different radiation conditions into account, a solar energy unit, Q_{UV}, which estimates the accumulated UV energy in the photoreactor per unit of volume of treated water for a given time during the experiment, is employed. This normalizes the energy available for the photocatalytic reaction under natural sunlight. The intensity of the solar UV radiation was measured by a global UV radiometer (Mod. CUV3, KIPP&ZONEN, The Netherlands) with a typical sensitivity of 264 μV/W per m^2, which provides data in terms of incident W_{UV}/m^2. This is used to calculate the total UV energy received per unit of volume Q_{UV} with Eq. (2) [18], where t_n is the experimental time for n-sample, $\overline{UV}_{n-1}$ is the average solar ultraviolet radiation measured during the period ($t_n - t_{n-1}$), A_r is the illuminated surface, and V_t the total water volume.

$$Q_{UV} = \sum_n \overline{UV}_{n-1} \frac{A_r}{V_t} (t_n - t_{n-1}) \quad (2)$$

2.6. Water quality

Experiments were carried out using distilled water and also natural well water so that the inactivation environment would be chemically similar to the irrigation water where phytopathogenic fungi might appear. Water was taken from the PSA well at a depth of approximately 200 m. The concentration of naturally occurring organisms determined by plate count enumeration using LB agar was found to be 100–200 CFU/mL. These organisms were identified as non-coliforms and non-enteric in nature due to their presentation as either irregular, colorless colonies or after complete lack of growth on Endo agar. No other fungal species were detected by the

Table 2
Physical and chemical properties of the well-water.

Cl^-	355 mg/L	Na^+	370 mg/L
NO_3^-	22 mg/L	$NH4^+$	6 mg/L
SO_4^{2-}	329 mg/L	K^+	11 mg/L
F^-	1 mg/L	Mg^{2+}	64 mg/L
Br^-	2 mg/L	Ca^{2+}	122 mg/L
PO_4^{3-}	0.5 mg/L	HCO_3^-	500 mg/L
pH	7.3	Conductivity	2300 μS/cm
Turbidity	1–2 NTU	Bacteria	100 CFU/mL

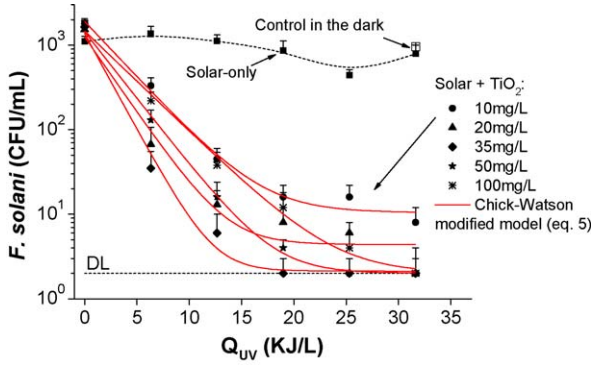

Fig. 2. Viable *F. solani* spores over time in distilled water under natural sunlight in presence of TiO_2 at 10, 20, 35, 50, and 100 mg/L and in the absence of TiO_2 ('solar-only') in the bottle reactor. Lines show the fitting of the experimental data with the kinetic model represented by Eq. (5). Mean solar UVA irradiance during all solar exposure tests: 37 W m^{-2}. Control in the dark with TiO_2 (20 mg/L). DL is the detection limit for the experiments, 2 CFU/mL.

same malt agar detection method used for the experiments. So that all the experimental results could be compared, a single batch of 200 L of well water was withdrawn at once so the same stock of water could be used in all the experiments, and no variation in the composition of the natural well water was possible. Table 2 shows the general physical and chemical parameters of the water used in the experiment series.

Turbidity, measured using a Model 2100N Hach (U.S.A.) turbidimeter, was between 1 and 2 NTU in all the experiments. We did not find any Fe in the water (UV–vis measurements, detection limit 0.05 mg/L). Ion analysis was done by ion chromatography (IC) for anions with a Dionex DX-600 system and for cations with a Dionex DX-120 system. TOC and TC were analyzed by a Shimadzu TOC-5050 analyzer. The pH was measured by a pH electrode (WTW, Germany).

3. Results and discussion

3.1. Disinfection of F. solani in solar bottle reactors with distilled water

Fig. 2 shows that suspensions of *F. solani* spores in water are susceptible to solar photocatalytic disinfection with TiO_2 under natural sunlight in a small volume of distilled water (200 mL), in agreement with previous findings [15,19]. These results show an effective 3-log reduction of fungal spores (from ~10^3 CFU/mL to the detection limit) after 5 h exposure. All the controls with the TiO_2 concentrations tested in the dark remained stationary. Only the 20-mg L^{-1} sample is presented here (the rest of data not shown). Mere solar radiation does not show any inactivation of fungal spores at all.

Due to the complex mechanism of the disinfection processes, the kinetic analysis of the photocatalytic bacterial inactivation has been usually carried out using empirical equations. That is the case of the disinfection model reported in the literature by Chick–Watson [20,21]. In photocatalytic processes, the general expression the Chick–Watson equation is reduced to:

$$\mathrm{Log}\left(\frac{N}{N_0}\right) = -k \cdot t \tag{3}$$

where N/N_0 is the reduction in the concentration of microorganism, k is the disinfection kinetic constant, and t is the time of treatment. For solar processes the Chick–Watson's law modified to our experimental conditions, where time is replaced by the amount of solar UVA energy received during the experiments per unit of volume (Q_{UV}) to make possible further comparison with results obtained in other solar reactors:

$$\mathrm{Log}\left(\frac{N}{N_0}\right) = -k' Q_{UV} \tag{4}$$

In many cases, the disinfection rate remains constant from the beginning of the reaction and decrease after a period of treatment, when the concentration of microorganism is very low. Then a modification of the Chick–Watson could be applied [22], according to the following two-parameters expression. This modified Chick–Watson model could describe a pseudo-first order kinetics and the existence of a tail at the end of the reaction. The corresponding time-equation modified to our experimental conditions is the following equation:

$$N = (N_0 - N_{res}) \cdot \exp(-k'' Q_{UV}) + N_{res} \tag{5}$$

where N_{res} is the residual concentration (tail region of the graph) of microorganism. Data of different fittings done using Eqs. (4) and (5) are shown in Tables 3 and 4.

The last stage of photocatalytic inactivation, as shown in Fig. 2, is marked by strong attenuation of the inactivation rate. This could be due to: (i) competition for the catalyst, light and hydroxyl radicals of dead spores and by-products generated by the fungicidal process. (ii) The probability of hydroxyl and other radicals coming in contact with viable spores of *F. solani* is lower at the end than at the beginning of photocatalytic treatment, since at the end of treatment very few culturable spores remain. Fig. 2 shows how the concentration of viable *F. solani* spores diminishes from 1000 to 10 CFU/mL during the first 2.5–3 h of photocatalytic treatment (depending on catalyst concentration) and the concentration of viable colonies decreases very slowly during the

Table 3
Inactivation rate constants (k') and correlation coefficients (R^2) found by linear regression of Eq. (4) for photocatalyis tests done in bottle and solar CPC reactors under natural sunlight at different TiO_2 concentrations.

Bottle reactor and distilled water (Fig. 2)			CPC photoreactor and distilled water (Fig. 3)			CPC photoreactor and well water (Fig. 4)		
Conc. TiO_2 (mg L^{-1})	k' (L kJ^{-1})	R^2	Conc. TiO_2 (mg L^{-1})	k' (L kJ^{-1})	R^2	Conc. TiO_2 (mg L^{-1})	k' (L kJ^{-1})	R^2
10	0.111 ± 0.009	0.98	10	0.156 ± 0.014	0.98	50	0.142 ± 0.004	0.999
20	0.16 ± 0.03	0.99	50	0.22 ± 0.02	0.98	**100**	**0.32 ± 0.02**	0.999
35	**0.19 ± 0.04**	0.99	**100**	**0.40 ± 0.07**	0.99	250	0.20 ± 0.03	0.97
50	0.137 ± 0.012	0.98	250	0.34 ± 0.03	0.99			
100	0.104 ± 0.009	0.99	500	0.280 ± 0.002	0.9999			

The bold numbers indicate the highest rate constant found.

Table 4
Inactivation rate constants (k''), residual concentration of spores (N_{res}) found by the method of Least Sum of Squared Errors of Eq. (5) for photocatalyis tests done in bottle and solar CPC reactors under natural sunlight at different TiO_2 concentrations.

Bottle reactor and distilled water (Fig. 2)			CPC photoreactor and distilled water (Fig. 3)			CPC photoreactor and well water (Fig. 4)		
Conc. TiO_2 (mg L^{-1})	k'' (L kJ^{-1})	Log_{10} (N_{res})	Conc. TiO_2 (mg L^{-1})	k'' (L kJ^{-1})	Log_{10} (N_{res})	Conc. TiO_2 (mg L^{-1})	k'' (L kJ^{-1})	Log_{10} (N_{res})
10	1.9 ± 0.2	1.02 ± 0.09	10	1.47 ± 0.04	1.59 ± 0.02	50	1.3 ± 0.2	2.10 ± 0.05
20	2.6 ± 0.6	0.6 ± 0.2	50	2.07 ± 0.07	0.97 ± 0.03	**100**	**2.52 ± 0.07**	**0.80 ± 0.02**
35	**3.3 ± 0.4**	**0.33 ± 0.09**	**100**	**3.3 ± 0.4**	**0.33 ± 0.09**	250	2.1 ± 0.2	1.30 ± 0.04
50	2.30 ± 0.08	0.30 ± 0.04	250	2.4 ± 0.2	0.44 ± 0.09			
100	1.7 ± 0.1	0.3 ± 0.1	500	1.8 ± 0.2	0.6 ± 0.1			

The bold numbers indicate the highest rate constant found.

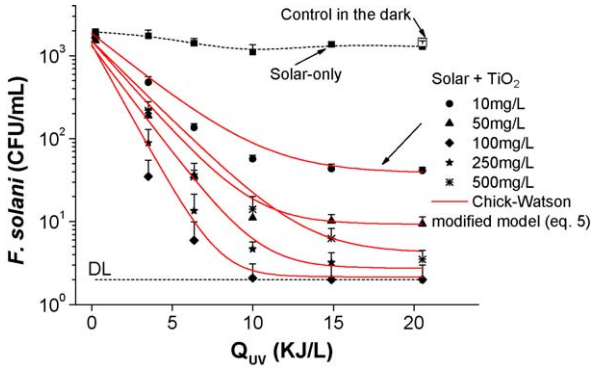

Fig. 3. Viable *F. solani* spores over time in distilled water under natural sunlight in presence of TiO_2 at 10, 50, 100, 250, and 500 mg/L and in the absence of TiO_2 ('solar-only') in the CPC solar reactor. Lines show the fitting of the experimental data with the kinetic model represented by Eq. (5). Mean solar UVA irradiance during all exposure tests: 38 W m^{-2}. Control in the dark with TiO_2 (250 mg/L). DL is the detection limit for the experiments, 2 CFU/mL.

subsequent 2.5–3 h of treatment. This confirms that the best photocatalytic inactivation rate is found with 35 mg L^{-1}, as expected for this experimental configuration, since the behavior of light inside the reactor is a key factor in photocatalysis.

3.2. Solar CPC reactors with distilled water

Fig. 3 shows the survival of *F. solani* spores in distilled water in the CPC reactor during photocatalytic disinfection experiments with different concentrations of TiO_2 (10, 50, 100, 250, and 500 mg L^{-1}) and the control tests in the dark and under sunlight. Initial concentrations of fungal spores are observed to be very similar in all experiments. Dark survival in the CPC reactor in the presence of 250 mg/L TiO_2 shows that the flow regime in the reactor and contact with the catalyst alone have no negative effect on the fungal spore concentration.

In previous experiments with fungal spores in this reactor at a 10-L/min flow rate (results not shown) spores and TiO_2 particles settled forming sediment. The fungus cell walls are expected to be negatively charged, as are other microorganisms in water with few exceptions [29]. At the slightly acid pH of 5.5 in distilled water, the catalyst still had a positive surface charge [30,31] and stuck to the cell wall of the fungus spores, increasing the weight of the aggregates, and a flow rate of 10 L/min or lower is not enough to keep them in suspension, leading to a loss of catalyst and spores from sedimentation. The strong tendency of TiO_2 to adhere to the fungal spores was already demonstrated in our previous work [15], in which TiO_2 completely covered the spore surface during the 5-h experiment. Nevertheless, we were able to completely avoid this sedimentation by increasing flow rates in the reactors. So the experiments in the CPC reactor were run at 20 L/min and all spore inactivation under sunlight and in presence of TiO_2 is therefore due to the photocatalytic disinfection process, not to sedimentation or other loss in the dark.

The blank test under an average solar irradiation of 35 W/m^2 shows that sunlight alone has no effect on the survival of the fungal spores and did not reduce the fungal concentration. TiO_2 has a completely different mode of action [24,25]. TiO_2 attaches itself to the spore cell walls and oxidizes lipids and proteins, and when solar UV light enters the cell, it is absorbed by intracellular chromophores causing oxidative stress [32,33,34].

Fig. 3 shows that the concentration of viable *F. solani* spores diminishes from about 2000 CFU/mL to the detection limit (2 CFU/mL) after 3 h of photocatalytic treatment with only 100 mg-TiO_2/mL. This result again corroborates that the concentration of catalyst yielding the best photocatalytic inactivation rate (Tables 3 and 4) can be estimated with Eq. (1), which predicts 83 mg L^{-1} for this reactor and optical path length.

Comparison of the results in the bottle reactor and in the CPC prototype, shows that the solar CPC reactor makes more efficient use of the solar radiation for water disinfection, since less energy is needed to treat a given volume of polluted water. It is also worth mentioning the importance of using the system's optimal TiO_2 concentration and a high flow rate for best disinfection efficiencies. The highest inactivation rates (k', and k''; Eqs. (4) and (5), Tables 3 and 4) estimated in both systems under similar radiation and water conditions are also reached in the CPC system.

The CPC prototype design has the disadvantage of requiring piping and a recirculation tank, which add unilluminated parts to the reactor system. In the case of our CPC reactor only 4.7 L of the 14-L total volume could be illuminated. These dark parts of the reactor make it necessary to irridiate the fungal spores longer than in completely illuminated systems. Water must also be agitated for homogeneous mixing of the catalyst to provide good contact between fungal spores and catalyst. Nevertheless the use of CPC systems still represents a significant improvement over the 250-mL bottle reactors. Photocatalytic water disinfection for the use and reuse of irrigation water is only of interest on large scales of liters or cubic meters. With CPC plants, both options are possible, because it is possible to upscale the process by increasing the number of CPC modules.

3.3. Solar CPC reactors with natural well water

Fig. 4 shows the effect of catalyst concentration in the CPC system during experiments performed with TiO_2 in natural well-water. TiO_2-based disinfection was achieved at all test concentrations (50, 100 and 250 mg/L). The disinfection yield is observed to increase with increasing concentration from a 1.2 log-reduction at 50 mg/L to almost 2.5 log at 100 mg/L. On the contrary, when the concentration is increased further from 100 to 250 mg/L, the effect is the opposite, decreasing from a 2.5 to a 1.9-log reduction.

The 50, 100, and 250 mg/L test concentrations show that, in fact, disinfection follows the expected tendency for concentration, reaching the best disinfection yield at 100 mg/L. As mentioned

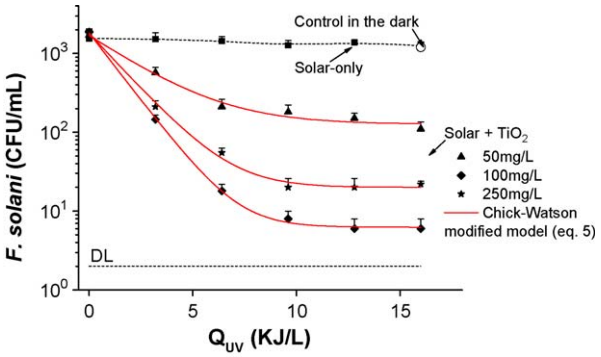

Fig. 4. Viable *F. solani* spores over time in natural well water under natural sunlight in presence of TiO_2 at 50, 100, and 250 mg/L and in the absence of TiO_2 ('solar-only') in the CPC solar reactor. Lines show the fitting of the experimental data with the kinetic model represented by Eq. (5). Mean solar UVA irradiance during all exposure tests: 32 W m^{-2}. Control in the dark with TiO_2 (250 mg/L). DL is the detection limit for the experiments, 2 CFU/mL.

above, in all cases (Figs. 2–4), the last stages of photocatalytic inactivation are strongly attenuated.

In the three cases studied, the initial inactivation rates (Table 3) were lower with well water than with distilled water. This may be due to the very high carbonate/bicarbonate content in the water. In natural water and wastewater subjected to AOPs, oxidation of contaminants initiated by $CO_3^{-\bullet}$ is always in competition with oxidation by hydroxyl radicals and, depending on the process, oxidation by other oxidizing species, or photo transformation by UV light [35]. $CO_3^{-\bullet}$ formation rates cannot exceed those of hydroxyl radicals, while the main known scavengers of both are dissolved natural organic matter and, if present, hydrogen peroxide. The high carbonate ($CO_3^{-\bullet}$)/bicarbonate (HCO_3^-) content in the well water we used could be a limiting factor for the photocatalytic process. HCO_3^- reacts with the hydroxyl radicals, producing the less reactive anion radical $CO_3^{-\bullet}$ (Eqs. (6) and (7)). This radical shows a wide range of reactivity with organic molecules, but is mainly a selective electrophilic reagent, and its reactions are slower than those of $^\bullet$OH. Moreover, HCO_3^- is little photoabsorptive, which protects bacteria from light. This screening effect keeps light from penetrating the bacterial suspension [36].

$$^\bullet OH + HCO_3^- \rightarrow CO_3^{-\bullet} + H_2O \quad (6)$$

$$^\bullet OH + CO_3^{2-} \rightarrow CO_3^{-\bullet} + OH^- \quad (7)$$

Carbonates cannot be considered as the sole compound responsible for inhibition of the disinfection rate. It should also be considered that the cells could be stressed as a result of increasing osmotic pressure in the distilled water and therefore be more susceptible to disinfection [23].

In turbid water, the optimal concentration of TiO_2 may be lower, due to additional shadowing caused by light absorption and scattering by turbid material. However, even though the turbidity of the well water used here was a low 5 NTU, the disinfection yield was lower for experiments done with natural well water than with distilled water.

The concentrations of oxygen in both systems (bottle and CPC reactors) were measured. In all cases the values were near the concentration of saturation of dissolved oxygen in water for the temperature. Thus, this factor cannot limit the reaction rate.

This work is one of the first contributions which demonstrate the capability of solar photocatalytic treatment to disinfect water containing phytopathogens of high incidence in intensive agriculture. This early research step is necessary to develop new advanced methods of water disinfection. The final application of this process to recover and reuse water in agriculture needs more knowledge and innovation; since slurry based TiO_2 reactors cannot be used without a solution to recover the catalyst from treated water.

4. Conclusions

The use of solar photocatalysis with TiO_2 suspended in water has been tested with distilled and natural well water under natural sunlight. On completely sunny days, inactivation is faster in the system with distilled water than in natural well water.

A 14-L solar CPC prototype has been shown to have a better disinfection yield than a simpler solar bottle reactor due to more efficient use of the sunlight by the CPC mirrors.

The concentration of titanium dioxide yielding the best inactivation rates found experimentally can also be estimated using light extinction equations. The optimized experimental concentration for natural well water with low turbidity (5 NTU) is still very similar to the one calculated, 83 mg/L for a 4.6-cm inner tube diameter using a CPC system.

The experimental results with distilled and natural well water show the limiting effect of carbonates/bicarbonates. Therefore, upscaling a small prototype photocatalytic system like ours involves adjusting the flow regime, the irradiated volume, catalyst concentration, etc.

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