

SOLAR PHOTOCATALYTIC WATER DISINFECTION. CASE STUDY OF *FUSARIUM* SPORES

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ABSTRACT

This contribution aimed to present our recent results on water disinfection using solar energy to promote the following photocatalytic processes: TiO₂/UVA, photo-Fenton, and H₂O₂/UVA, at pilot plan scale. This work reports the ability of solar photocatalysis to inactivate *Fusarium* fungal spores in a solar bottle reactor and in a 60 L CPC prototype reactor. Inactivation of *Fusarium* sp spores by titanium dioxide (Degussa P25) was evaluated in distilled and natural well water. Three different spore of *Fusarium*: microconidia, macroconidia and chlamydospores were individually evaluated to determine whether there were differences in resistance to the photocatalytic treatment. The results showed that chlamydospores were the most resistant, followed by macroconidia, and finally microconidia were the most sensitive. Solar H₂O₂/UVA processes were experimentally studied using *Fusarium* chlamydospores (the most resistant type of spore) as model of pathogen. Distilled water, well water and simulated effluent of a municipal wastewater treatment plant were used as water matrixes. Experimental results showed that *F. equiseti* were inactivated with 10 mg L⁻¹ of H₂O₂ in a 60 L CPC photoreactor. These results demonstrated that the use of low concentrations of hydrogen peroxide and CPC systems may be a good alternative for disinfection of resistant microorganisms in water.

Keywords

Solar photocatalysis; hydrogen peroxide; titanium dioxide, photo-Fenton; water disinfection.

INTRODUCTION

Advanced Oxidation Processes are a group of related processes which involve the generation of radical oxygen species which result in the oxidative degradation of pollutants in water. Advanced oxidation processes (AOPs) have been demonstrated to have biocidal properties which lead to use AOPs for disinfection of water as well. Among AOPs, heterogeneous semiconductor photocatalysis like TiO₂/UVA, photo-Fenton, and hydrogen peroxide/UVA may work in the presence of solar photons. TiO₂/UVA employs light activated semiconductor TiO₂ to produce radical oxygen species which can inactivate microorganisms. Photo-Fenton catalytic cycle is based on the generation of hydroxyl radicals through the addition of hydrogen peroxide to Fe(II)/Fe(III) salts in the presence of UV-Vis photons. The photolysis of H₂O₂ yields hydroxyl radicals when irradiated by photons of wavelengths lower than 300 nm. Nevertheless, solar radiation that reaches the Earth's surface contains a small fraction of UVB (280–320 nm) and most of the UVA (320–400 nm) spectrum. Due to the absence of UVC, the use of solar energy is inefficient for hydroxyl radical generation by the photolysis of H₂O₂. However, there are some publications reporting the killing effect of H₂O₂/UVA-Vis for several

microorganisms in water. Although the mechanism is unclear, there is evidence for a synergistic effect between near UV or visible light and hydrogen peroxide for the inactivation of microorganisms.

METHODS

Generation and quantification of *Fusarium*

The *Fusarium* genus was chosen as the model fungal spore for conducting the solar photocatalytic experiment because of it is highly resistant to chemical compounds and its worldwide distribution. Some species are plant pathogens and some are opportunistic infectious agents of humans and animals. It is characterized by producing three different types of spores called microconidia, macroconidia and chlamydospores. *Fusarium* strain used in this study is a wild strain originally isolated in the natural environment, belonging to the collection of the Department of Plant Production of the University of Almeria.

The spore production methodology used has been described elsewhere (Fernández-Ibáñez *et al*, Sichel *et al*, 2009). The isolates were transferred to the sporulation medium, agar (CULTIMED, Spain) containing potassium chloride (PANREAC, Spain) in Petri dishes exposed to UVC radiation from a mercury lamp (40 W) for 15–30 days at 25°C. Spores were recovered from the sporulation agar were recovered by washing the plates with distilled water. Spore concentration was determined by direct counting with a Neubauer plate (Brand, Germany), and diluted in the reactor to the desired spore concentration, which varied between $10^2 - 10^3$ CFU·mL⁻¹. The fungal concentration during solar experiments was measured using the plate counting technique. 50–250–500 µL of the sample were plated out on acidified malt agar (Sigma Aldrich, USA). The plates were incubated for 2 days at 28°C in the dark before counting.

Solar reactors

The solar bottle reactor (200 mL total volume) experiments were conducted as proof of test prior to solar CPC reactor. The use of solar energy with Compound Parabolic Collector (CPC) mirrors has been applied to develop solar pilot plants for decontamination of water polluted with hazardous organics contaminants. Recently CPC have been used for water disinfection yielding promising results to inactivate bacteria, protozoa and fungi, either through solar disinfection and/or solar photocatalysis.

The CPC reactor consists of two CPC mirror modules, each made up of ten 1500 mm-long, 2.5 mm-thick and 50 mm-outer-diameter borosilicate glass tubes. The irradiated collector surface is 4.5 m². Water is recirculated through the tubes to a 60 L-capacity tank by a centrifugal pump (150 Watts). pH, dissolved oxygen (DO) and temperature sensors are inserted in the dark part of the tubes and their corresponding values are continuously monitored throughout the experiment thanks to a data acquisition software (DESIN Instruments, S.A.). UV radiation was measured with a global UVA radiometer (295–385 nm) tilted 37°, the same angle as the reactor and as the local latitude. The radiometer provides data in terms of incident W/m². The inactivation results may be analysed as a function of accumulative energy per unit of volume (Q_{UV} , kJ·L⁻¹) received in the photo-reactor, and calculated by Equation 1 (Fernández-Ibáñez *et al*, 2009).

$$Q_{UV,n} = Q_{UV,n-1} + \Delta t_n \overline{UV_{G,n}} A_r / V_t; \quad \Delta t_n = t_n - t_{n-1} \quad (1)$$

RESULTS AND DISCUSSION

Figure 1 shows solar photocatalytic degradation of *Fusarium* spores in natural well water with 0, 50 and 100 mg·L⁻¹ of TiO₂. After 5 h of solar exposure, the spore concentration in the blank test only dropped from 1520 to 55 CFU·mL⁻¹, which is still above the detection limit. The test with 100 mg·L⁻¹ of TiO₂ shows that the spore concentration fell from 490 CFU·mL⁻¹ to the detection limit in 4 h of photocatalytic treatment at a Q_{UV} of 41.5 kJ·L⁻¹. 50 mg·L⁻¹ of TiO₂ achieved the detection limit within 4 h with a Q_{UV} of 41.2 kJ·L⁻¹ and was the best *Fusarium* spore inactivation.

Solar disinfection (without catalyst) is successful in this CPC reactor, which plays an important role in the disinfection rate (see 0 mg·L⁻¹ in Fig. 1) with natural water and also in distilled water (data not shown). The good performance of solar disinfection observed in all experiments done in the new CPC photoreactor can be attributed to increased continuous illumination time. This strong fungicidal effect of solar radiation in the absence of catalyst was not detected before in our former works (Fernández-Ibáñez *et al*, Sichel *et al*, 2009).

The best disinfection performance TiO₂ concentration estimated for this reactor and optical path length of 50 mg·L⁻¹ was confirmed with experimental results in Fig. 1, since the behaviour of disinfection obtained for 50 mg·L⁻¹ are very similar or better than those obtained for 100 mg·L⁻¹ and 250 mg·L⁻¹ of TiO₂. This behaviour can be due to mass transfer limitations when the spore concentration is too low, like the present case.

Figure 2 shows inactivation kinetic results of *Fusarium* in distilled (DW), well (WW) and simulated effluent (SE) water for the solar CPC reactor under solar light and H₂O₂ (10 mg·L⁻¹). Spores were completely inactivated from 180 CFU mL⁻¹ to the detection limit 2 CFU mL⁻¹ in DW after receiving a cumulative solar UV energy of 14.9 kJ L⁻¹. The spore concentration was reduced by 1.8 log in the WW case, from 570 to 5CFU mL⁻¹, for Q_{UV} = 28.7 kJ L⁻¹. In the case of SE, complete fungal inactivation, from 330 to the detection limit, was observed for Q_{UV} = 29.7 kJ L⁻¹.

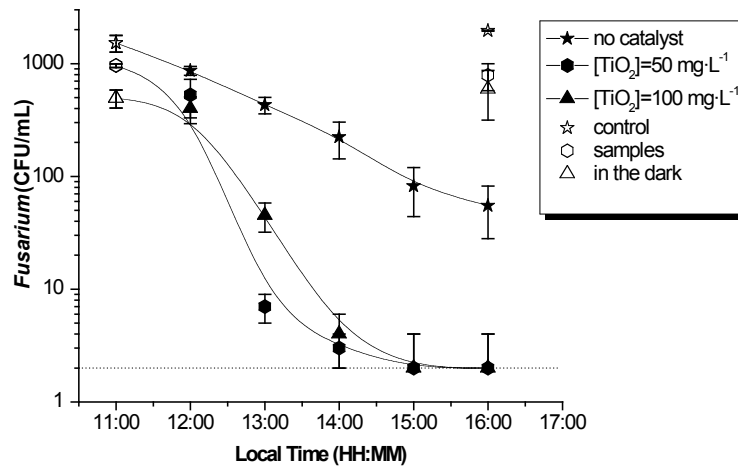


Figure 1. Viable *Fusarium* spores over local time in well water under natural sunlight in presence of TiO_2 in the solar CPC reactor.

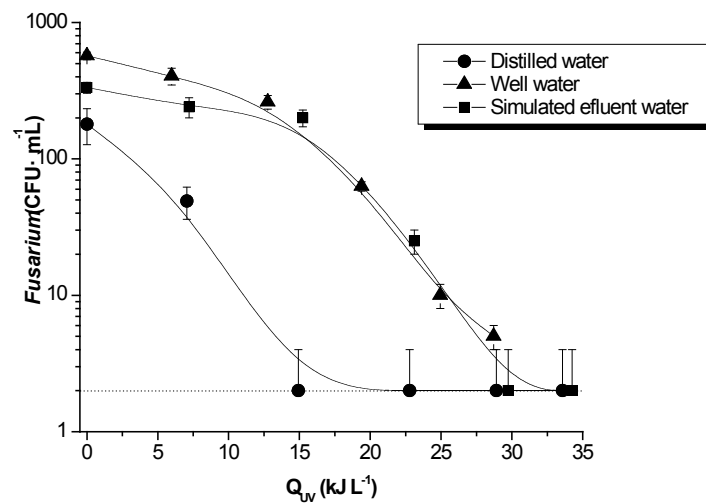


Figure 2. *Fusarium* disinfection using sunlight/ H_2O_2 (10 mg L^{-1}) in the CPC.

CONCLUSIONS

The solar TiO_2 treatment is a promising technique to inactivate phytopathogenic agents not only in distilled water but also in well water, although in well water the limiting effect of carbonates/bicarbonates makes the reactions less efficient. We have demonstrated that it is possible to upscale photocatalytic treatment for further reuse of irrigation water (hydroponic closed irrigation systems) when the irradiated collector surface of the CPC photoreactor is increased. This study also showed that adding small amounts of hydrogen peroxide ($10 \text{ mg}\cdot\text{L}^{-1}$) in the presence of solar radiation can disinfect water polluted with *Fusarium* spores. The efficacy of this process was successfully proven in the CPC reactor for DW, WW, and SE.

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