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Effect of UV solar intensity and dose on the photocatalytic disinfection of bacteria and fungi

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Abstract

The purpose of this work was to study the dependence of solar photocatalytic and solar water disinfection on solar irradiation conditions under natural sunlight. This dependency was evaluated for solar photocatalysis with TiO_2 and solar-only disinfection of three microorganisms, a pure *E. coli* K-12 culture and two wild strains of the *Fusarium* genus, *F. solani* and *F. anthophilum*. Photocatalytic disinfection experiments were carried out with TiO_2 supported on a paper matrix around concentric tubes, in compound parabolic collectors (CPCs) or with TiO_2 as slurry in bottle reactors, under natural solar irradiation at the Plataforma Solar of Almería (Spain). The experiments were performed with different illuminated reactor surfaces, in different seasons of the year, and under changing weather conditions (i.e., cloudy and sunny days). All results show that once the minimum solar dose has been received, the photocatalytic disinfection efficacy is not particularly enhanced by any further increase. The solar-only disinfection turned out to be more susceptible to changes in solar irradiation, and therefore, only took place at higher irradiation intensities.

Keywords: *E. coli*; *F. solani*; *F. anthophilum*; Solar energy; Photocatalytic disinfection; TiO_2

1. Introduction

Water quality and its sustainable supply are major worldwide concerns. Standards and controls avoiding contamination by microorganisms, especially pathogenic specimens, underlie the safety of drinking water. Depending on the final use, water requirements, such as the WHO Guidelines for drinking water, may be very strict. Water used in agriculture must also comply with minimum safety standards, since irrigating water is a vehicle for plant pathogens and contagion, especially in intensive greenhouse agriculture, where the reuse of irrigation water is often limited due to contamination by phytopathogens. Water that does not meet these standards must be disinfected before its recirculation.

Because of its cheap, easy application, chlorination is often used for disinfection, however, among its negative effects are the appearance of trihalomethanes (THMs) as the by-products of its reaction with organic matter, phytotoxicity, and an unpleasant taste when used for drinking water [1,2]. Both the thermal energy of sunlight and its germicide properties have recently been used for disinfection [3,4]. In addition to large-scale applications in solar reactors [5–7], research for solar disinfection in recent years has often focused on small-volume (1.5 L) UV-light-transparent plastic bottles as batch reactors for domestic treatment of drinking water in areas with high solar irradiance [3,8]. Called the SODIS treatment, it has been proven successful for a wide range of microorganisms including bacteria, fungus spores, cysts, etc. [4,9,10].

Nevertheless, this type of solar disinfection is limited in applications with high volumes of water or more resistant microorganisms, and may therefore be enhanced by the addition of a photocatalyst semiconductor. This advanced oxidation technology can be deployed for air and water treatment using TiO_2, an already well-analyzed, low-cost photocatalyst. The wide range of TiO_2 applications was recently reviewed by Fujishima [11]. Among its other applications, TiO_2 for the treatment of different types of water contamination has been studied in depth [12].

When TiO_2 is excited by the energy of near UV-radiation (<400 nm) a photocatalytic reaction that generates electron–hole pairs on the semiconductor surface takes place [13]. In the presence of water and oxygen, hydroxyl radicals ($^{\bullet}OH$) are

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formed [14]. Hydroxyl radicals are known to be strong, not very selective oxidizing agents. Furthermore, water treatment with TiO_2 photocatalysis does not require the addition of consumable chemicals. Killing microbial cells with a photoexcited semiconductor powder was first reported by Matsunaga *et al.* [15]. Since then, an increasing amount of research has contributed to the development of new materials, supported photocatalysts, photoreactors and procedures for water disinfection. Results suggest that oxidative damage first takes place on the cell wall, where the TiO_2 photocatalytic surface makes contact with the cell [16,17]. Maness presented evidence of peroxidation of the polyunsaturated phospholipid component of the lipid cell membrane, which produces major life-threatening damage leading to a loss of essential functions, such as respiratory activity, and consequently to cell death [16]. Although it is uncertain which reactive oxygen species are directly involved in the photokilling process, the main reactive oxygen species (ROS) are OH radicals [18], $O_2^{\bullet -}$ and H_2O_2 [19]. Many publications have focused on the application of TiO_2 photocatalytic disinfection at laboratory scale [20], however those concentrating on the use of solar energy [21,22], or on pilot-plant scale applications under natural sunlight are scarce [5,6,23–25]. Some work has also been published on the successful disinfection of water from real sources such as rivers, lakes and wells [26,27].

Disinfection yield with chemicals depends on the concentration of the bactericidal agent and contact time with the microorganisms [28]. In UV-disinfection systems, the yield depends on UV-lamp irradiation time (254 nm), characterized by their performance [29]. The most common way of comparing the resistance of different types of microorganisms to a UV-disinfection system is by determining the ''UV dose'' in kJ m^{-2}, defined as the product of the UV intensity, expressed as UV irradiance (W/m^2) [30], and irradiation time needed for a given disinfection level, as measured by the decrease in colony forming units (CFU) [31,32,9,10]. The efficacy of solar systems, in which the sun is the source of photons at a wavelength of 300 nm to approximately 1400 nm [33], can also be characterized by the disinfecting ''solar UV dose'' (kJ m^{-2}). In solar reactor systems, the unit considered is often the accumulated solar UV energy (kJ L^{-1}) received during photocatalytic disinfection [25,13,6]. Some authors consider the global solar spectrum when comparing natural and simulated sunlight disinfection performance [4]. Nevertheless, the most suitable way of comparing solar disinfection system efficiency (with or without catalyst) still remains undecided. This is probably due to the changeable irradiation conditions of sunlight and the limited knowledge of the mechanisms governing the solar-only and solar photocatalytic (TiO_2) disinfection processes. Even if only the definition of specific criteria is considered essential, very few contributions have focused on the issue of comparing solar photocatalytic disinfection experiments by the solar dose or solar energy received, as do Rincón and Pulgarin [26].

The goal of this work was to determine disinfection performance by the solar dose and energy per unit of volume received under very different experimental conditions and microorganisms. This was assessed in two reactor systems: (a) a CPC solar reactor pilot plant with *E. coli* and (b) bottle reactors with the fungi, *Fusarium solani* and *Fusarium anthophilum*. Three different types of solar radiation experiments were studied: (i) at different times on sunny days close together in the same season and (ii) in different seasons; and (iii) solar tests done on days close together, but under different weather conditions (cloudy and sunny).

2. Experimental methods

2.1. Bacteria strain and quantification

Escherichia coli K-12 was inoculated in a Luria broth nutrient medium (Miller's LB Broth, Sigma–Aldrich, USA) and incubated at 37 °C by constant agitation under aerobic conditions. Growth was monitored by optical density measurement at 600 nm. Bacteria were collected after 24 h of stationary-phase incubation, yielding a concentration of 10^9 CFU/mL. *E. coli* suspensions were centrifuged at 3000 rpm for 10 min and washed three times with saline solution (0.9% NaCl). Finally, the bacteria pellet was resuspended in distilled water and diluted in the 14-L photoreactor tank to the cell density required for the initial concentration. The reactor was kept running in darkness for 15 min to allow bacteria to adjust to the environment and come to a homogeneous suspension before exposure. Then a 0-min sample was taken and kept in the dark as a ''control sample''. After 90 min this ''control sample'' and the 90-min reactor sample were simultaneously replated. The samples taken during the experiment were serially diluted in distilled water and plated 16 times (16 × 10 μL) on Luria agar (Sigma–Aldrich, USA). Colonies were counted after incubation for 24 h at 37 °C. Where fewer than 10 colonies per plate were observed, 250 μL of the sample were plated for a detection limit of 4 CFU/mL.

2.2. Fungal strain and quantification

The fungi used were *Fusarium solani* and *Fusarium anthophilum*. Both fungi were chosen for their importance as pathogenic fungi in agriculture and their medium (*F. solani*) and low (*F. anthophilum*) resistance to photocatalytic disinfection as found in previous work [34]. The strains were original wild fungi obtained from soil cultures in Almería (southern Spain). The fungal colonies were transferred to an agar sporulation medium containing sodium and potassium chloride in Petri dishes exposed to UV-C radiation from a mercury lamp (40 W) for 15 days at 25 °C to produce the required number of spores (10^5–10^7 CFU/plate) [34]. Our disinfection work was based on spore inactivation as spores are the most resistant fungal life form. The spores were detached from the mycelia and agar by washing the plates with distilled water. The suspension obtained was homogenized by mechanical agitation, and the concentration was determined by direct count using a phase contrast microscope. The initial adjusted experimental concentration was approx. 10^3 CFU/mL. 50–250-μL samples of the water were plated out using the spread-plate technique on acidified (pH4) malt agar (Sigma–Aldrich, USA).