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Disinfection of urban effluents using solar TiO_2 photocatalysis: A study of significance of dissolved oxygen, temperature, type of microorganism and water matrix

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ABSTRACT

The enhancement of current technologies used to treat polluted water is one of the most important challenges in water research. The application of physico-chemical treatments could reduce the load of chemical and biological pollutants present in WW reducing the pressure over water requirements, allowing the reclaim of the treated water. Advanced Oxidation Processes (AOPs) and, in particular, photocatalysis using titanium dioxide (TiO_2) have shown a great potential for chemicals removal as well as for pathogens reduction in water. Moreover, the use of solar Compound Parabolic Collectors (CPC) reactors has been also shown to be very effective for water treatment purpose by solar photocatalysis. Nevertheless, the effects of some key parameters in photocatalytic disinfection have not been already investigated at pilot scale in solar reactors; like dissolved oxygen concentration, water temperature, water matrix composition and the type of microorganism. The roles of these parameters in photocatalytic processes are individually known for chemicals degradation, but their relative significance in water photocatalytic disinfection has been never studied at pilot scale. The aim of this work was to investigate the influence of these parameters on the disinfection efficiency using a solar 60 L-CPC reactor with suspended TiO_2 (100 mg/L). The following variables were experimentally evaluated: injection of air in the reactor (160 L/h); different controlled temperatures (15, 25, 35 and 45 °C); two very different models of water pathogen, *Escherichia coli* (model of fecal water contamination) and *Fusarium solani* spores (a highly phytopathogenic fungus); and the chemical composition of the water comparing urban WW effluents (UWWE) and simulated urban WW effluent (SUWWE). The increase of water temperature (from 15 to 45 °C) had a benefit on the disinfection rate for both pathogens in all the experimental conditions evaluated. The air injection led to an important enhancement on the inactivation efficiency, which was stronger for *F. solani* spores, the most resistant microorganisms to TiO_2 photocatalysis. The composition of the water matrix significantly affected the efficiency of the photocatalytic treatment, showing a better inactivation rate in SUWWE than for UWWE.

1. Introduction

Recently, big efforts have been done to develop alternative water treatment systems to decontaminate wastewater (WW) using processes based in reactive oxygen species (ROS). The photocatalytic treatments which use solar light have gained great attention as they produce ROS to destroy organic contaminants and kill microorganisms in water with very low energy consumption. In the last decade, a number of articles have demonstrated the capability of solar photocatalysis to decontaminate and disinfect water polluted by organic and biological agents [1].

Reuse of treated WW is an alternative resource of water since freshwater scarcity and lack of access to safe water is a human sizeable problem today [2]. Wastewater must be treated before discharge or for restricted reuse; it may contain industrial and agriculture chemical pollutants and also a wide range of pathogens, i.e. bacteria, viruses and fungi [3].

Agriculture is probably the most affected field by fungal pathogens like *Fusarium* spp. which is especially harmful in intensive agriculture [4]. *Fusarium* has been reported to be highly

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resistant to chemical and photocatalytic treatments due to its spores [5,6]. *Fusarium* spp. have been associated with human disseminated infections which recently has increased, particularly in patients with underlying immunosuppressive conditions, as leukemia, cancer or AIDS patients [7]. On the other hand, WW is frequently loaded with *Escherichia coli*, fecal indicator organism whose presence in water indicates possible contamination with other enteric pathogens like *Salmonella*, *Shigella* or *Yersinia*, enteric bacteria that could cause gastrointestinal diseases that generally presents with diarrhea [8].

Advanced Oxidation Processes (AOPs) are a good alternative for the traditional disinfection methods which are limited and have some drawbacks. AOPs are based on physicochemical processes that produce powerful oxidizing species, mainly hydroxyl radicals (•OH), in situ. Heterogeneous photocatalysis with the semiconductor TiO_2 is an AOP that has been used to decontaminate water containing hazardous pollutants and for disinfection of some pathogens [9]. TiO_2-photocatalysis in water use the UVA radiation (λ < 387 nm) to excite the photocatalyst, that in presence of oxygen and in contact with the water produces •OH (summarized in Eqs. (1) and (2)). Hydroxyl radicals have a high reactivity and therefore a short half-life. Thus the process will be favored when TiO_2 is adsorbed over (or very close to) the cell wall of the microorganism and this is induced by different electrical charge of microorganism and catalyst [10]. The oxidative action alters cell components and their functionality, causing a loss of cell integrity, changing the permeability and diffusion of cellular components to the medium, ending in cell death.

$$TiO_2 + h\nu \rightarrow e^-_{BC} + h^+_{BV} \quad (1)$$

$$H_2O + h^+_{BV} \rightarrow {}^{\bullet}OH + H^+_{aq} \quad (2)$$

$$O_{2(ads)} + e^-_{BC} \rightarrow O^{\bullet -}_{2(ads)} \quad (3)$$

However, if oxygen concentration is low in the system, electrons are not caught (Eq. (3)) and then e^-/h^+ pairs can recombine and inhibit the production of •OH. To avoid this, the presence of oxygen is always required for proper efficiency of the photocatalytic process. Moreover, $O_2^{\bullet -}$ is also oxidant (ROS) and therefore acts as a disinfectant causing DNA damage [11].

A number of articles have demonstrated the capability of TiO_2 photocatalysis for bacteria, viruses, protozoa, prions or fungi inactivation in water [12,13]. Rincón et al. demonstrated the benefits of using TiO_2 for disinfecting distilled and lake water polluted with *E. coli* [14]. Seven et al. inactivated *E. coli*, *Pseudomonas aeruginosa*, *Staphylococcus aureus*, *Candida albicans* and *Saccharomyces cerevisiae* using TiO_2 with very good results in all cases [15]. Our group has also studied the photocatalytic susceptibility of a variety of *Fusarium* spp. and have demonstrated that TiO_2 photocatalysis can be used with CPC reactors for eliminating pathogens present in water [16,17].

Water temperature has direct effects on disinfection efficacy, but it has not investigated up to date in photocatalytic water disinfection. The disinfecting effect of high temperatures is well known as pasteurization. Thermal increasing beyond the optimal temperature, drastically reduce the viability of microorganisms due to loss of integrity of proteins, enzymes and genetic material. The optimal temperature for the most bacteria is between 35 and 40 °C; while it is around 28 °C for the most of the fungus [18]. Moreover, the lethal action of solar mild heat over bacteria has been investigated at temperatures between 40 and 52 °C [19–21]. Given the importance of temperature in microbial metabolism and disinfection, up to our knowledge there is no research done on the effects of temperature of photocatalytic disinfection of water. This contribution will experimentally undertake this aspect at pilot scale with controlled temperature.

The role of oxygen in metabolic processes is already well known. Oxygen crosses membranes freely and ROS are generated internally due to aerobic metabolism. This increases the oxidative stress inside cells [22]. It has been proven that an increase of dissolved oxygen (DO) in water induced by proper agitation of batch containers of SODIS accelerates the disinfecting effect of solar radiation [23]. Studies by Reed et al. [24] found a 4–8 times faster inactivation rate of fecal bacteria in oxygenated water, compared to deoxygenated water [25–27]. Furthermore, these authors demonstrated that if water was bubbled with nitrogen before to solar exposure, it resulted in worst inactivation efficiency than aired samples [24]. Therefore, oxygen was confirmed as essential to disinfect fecal coliforms in batch solar disinfection process. In solar photocatalytic disinfection the DO plays also an important role. Rincón et al. reported an increased photocatalytic inactivation of *E. coli* and *Bacillus* spp. in water with conditions of oxygenation >8 mg/L (supplying oxygen as bubbled pure O_2) [28]. This work confirmed the importance of oxygen even for disinfection in non-controlled temperature conditions at small scale (4 L). The present work aims to experimentally evaluate this factor but with controlled temperature at pilot scale (60 L). The disinfection of contaminated SUWWE and UWWE with *Fusarium solani* and *E. coli* using solar photocatalysis with TiO_2 was evaluated at different temperatures (15, 25, 35 and 45 °C) with and without air injection in the solar reactor.

2. Materials and methods

2.1. Solar CPC pilot plant

The solar CPC pilot plant used consists of two CPC mirror modules titled 37° (Fig. 1a). Each CPC mirror module is made up of 10 borosilicate glass tubes of 1500 mm long, 2.5 mm thick and 50 mm outer diameter (UVA-transmission: 90%). The CPC mirror is made of highly reflective anodised aluminum with concentration factor CF = 1 (95% total reflectivity). The ratio of irradiated water (45 L) to total water (60 L) is 75%, with a CPC of 4.5 m^2. Water is recirculated through the tubes to a tank by a centrifugal pump (150W, Mod. NH-200 PS PanWorld, USA). Flow was controlled by a Yokogawa magnetic flow meter (Admag, RXF, Yokogawa Electric Corporation, Japan) at 30 L/min (turbulent flow; Reynolds: 16600) to avoid catalyst sedimentation. Online sensors for pH, DO and temperature (Crison, Spain) acquired the measurements during the tests (Fig. 1b). Temperature was controlled at: 15, 25, 35 and 45 °C using a heating electric resistance to increase the water temperature, and a cooling system (Fig. 1c). DO in the water was increased by two air pumps that inject air (160 L/h) at two equidistant points of the solar reactor system (Fig. 1a and b).

2.2. Water sources

Simulated urban WW treatment plant effluent (SUWWE) was used as a synthetic model of WW effluent with 25 mg/L of dissolved organic carbon (DOC). This water was chosen because it contains organic matter (urea, peptone and meet extract) [29]. The ionic content in this SUWWE was measured (Table 1).

Urban WW treatment plant effluent (UWWE) of Almería, El Bobar (Spain), was used as real effluent of a secondary treatment. UWWE was freshly collected from the treatment plant in the morning of each disinfection assay. Every UWWTE stock used was characterized and the average of the inorganic chemical compounds measured is shown in Table 1. The concentration of ions was measured with a Dionex DX-600 and Dionex DX-120 (California, USA) ion chromatographs for anions and cations.