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Effect of iron salt counter ion in dose–response curves for inactivation of *Fusarium solani* in water through solar driven Fenton-like processes

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ABSTRACT

The inactivation of *Fusarium solani* in water was assessed by solar driven Fenton-like processes using three different iron salts: ferric acetylacetonate ($Fe(acac)_3$), ferric chloride ($FeCl_3$) and ferrous sulfate ($FeSO_4$). The experimental conditions tested were [Fe] ≈ 5 mg L^{-1}, [H_2O_2] ≈ 10 mg L^{-1} and [Fe] ≈ 10 mg L^{-1}; [H_2O_2] ≈ 20 mg L^{-1} mild and high, respectively, and pH 3.0 and 5.0, under solar radiation. The highest inactivation rates were observed at high reaction conditions for the three iron salts tested at pH 5.0 with less than 3.0 kJ L^{-1} of accumulate energy (Q_{UV}) to achieve over 99.9% of *F. solani* inactivation. $Fe(acac)_3$ was the best iron salt to accomplishing *F. solani* inactivation. The modified Fermi equation was used to fix the experimental inactivation, data showed it was helpful for modeling the process, adequately describing dose–response curves. Inactivation process using $FeSO_4$ at pH 3.0 was modeled fairly with $r^2 = 0.98$ and 0.99 (mild and high concentration, respectively). $Fe(acac)_3$, $FeCl_3$ and $FeSO_4$ at high concentration (i.e. [Fe] ≈ 10 mg L^{-1}; [H_2O_2] ≈ 20 mg L^{-1}) and pH 5.0 showed the highest fitting values ($r^2 = 0.99$). Iron salt type showed a remarkable influence on the Fenton-like inactivation process.

1. Introduction

One of the main issues associated with adaptation of humankind to climate change is assuring the quality of water devoted for agricultural purposes. Food generation is the human activity with the highest water consumption, using up to 70% of available freshwater worldwide (95% in developing countries) (Food and Agriculture Organization [FAO], 2008). Water saving and storing have emerged recently not only as socially acceptable practices but also very important technologies that may support both food production and drinking water supplies in the near future. Water storage, however, includes several disadvantages, with pathogen accumulation being the most important considering further uses. Removal of pathogens in water has been historically carried out using different conventional water pretreatments for removal of different bacteria and viruses (Castillo-Ledezma et al., 2011). When used for agricultural purposes, stored or fresh water should be free of pathogens that may jeopardize the crops and, consequently, food production. Fungi are among the main phytopathogens frequently affecting agriculture. Some strains belonging to the *Fusarium* genus are capable of affecting plants as well as humans, particularly immune-compromised patients (Boutati and Anaissie, 1997; Anaissie et al., 2001; Fernández et al., 2009; El-Samra et al., 2009). *Fusarium* species, usually considered as resistant to many disinfecting agents, have been successfully inactivated in the past using solar heterogeneous photocatalytic disinfection process with TiO_2 as a photocatalytic semiconductor (Lonnen et al., 2005; Sichel et al., 2007a, b; Fernández-Ibáñez et al., 2009). Nevertheless, it has been found that homogeneous photocatalytic disinfection processes may possess interesting advantages for the inactivation of highly resistant microorganisms in water (Bandala et al., 2011a; Corona-Vasquez et al., 2012). In recent works, solar driven photo-assisted Fenton reaction has been demonstrated as a highly efficient, cost-effective technology for inactivating helminth eggs (Bandala et al., 2011b, 2012) and *Bacillus subtilis* spores (Bandala et al., 2009, 2011c), both considered capable of resisting extreme environmental conditions. In a recent paper, García-Fernández et al. (2012) achieved over 3-log cycles (99.9%) inactivation of

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Fusarium solani by the application of photo-assisted Fenton reaction using 2.5 mg L^{-1} of Fe^{3+} and 5.0 mg L^{-1} of H_2O_2 after 3 h of solar exposure (14.5 kJ L^{-1}); nevertheless, little is known about the process occurring during the inactivation process of *F. solani* using this technology.

The aim of this work is to evaluate the inactivation of *F. solani* spores by means of photo-assisted Fenton reaction using different iron salts in a solar reactor, to assess the effect of iron counter ion on the overall inactivation kinetics and to identify the best experimental conditions for the disinfection of water contaminated with this microorganism for agricultural or domestic use, as well as to model the inactivation process using the Fermi dose–response equation modified.

2. Material and methods

2.1. Reagents

All the reagents used in the experiments, ferric acetyl acetonate ($Fe(C_5H_7O_2)_3$) (Riedel-de Haën, Germany, commonly referred to as $Fe(acac)_3$), ferrous sulfate ($FeSO_4$) (Panreac Química SA, Spain), ferric chloride ($FeCl_3$) (Sigma-Aldrich, USA) and hydroxyl peroxide (H_2O_2, 35% stabilized, Riedel-de Haën, Germany) were ACS grade and used without any further purification. The *F. solani* strain used was obtained from the Spanish Type Culture Collection (CECT) with number CECT 20232.

2.2. Culture preparation

Spores of *F. solani* were collected by washing with sterile distilled water the mold surface previously grown in plates with sporulation agar (Bacteriological agar type Europe from Panreac Química SAU, Spain) and potassium chloride (J.T. Baker, Netherlands) and incubated under UV-C lamp for 15 days. From the suspension obtained, the spore concentration was quantified by direct counting in a Neubauer plate (Brand, Germany) using an optical microscope model Nikon Eclipse 50i (Japan), ensuring a spore concentration greater than 10^3 CFU mL^{-1}.

2.3. Photo-assisted pathogen inactivation

Experiments were carried out at Plataforma Solar de Almería (PSA), southern Spain, from May to July. All the experiments were conducted in individual systems using 250 mL sterile glass bottles as photoreactors. The bottles were filled with 200 mL of distilled water and submitted to solar radiation with an irradiated surface of 0.0095 m^2. Two initial working concentrations of iron salt were used (5 and 10 mg L^{-1}) and two of hydrogen peroxide (10 and 20 mg L^{-1}). Initial pH value was adjusted before starting the photocatalytic assessments to 3.0 or 5.0 using H_2SO_4 (0.1 M) or NaOH (0.1 M) as required. Once the pH was adjusted, the required amount of iron salt was added to the photoreactor and the mixture was stirred at 100 rpm for five minutes until complete iron salt dissolution. Then the spore suspension was added at a concentration of 10^3 CFU mL^{-1}, the reactors were stirred at 100 rpm for a few minutes, and the first sample ($t = 0$) was taken to determine the initial viable spores concentration. The sampling was performed at times $t = 0, 30, 60, 90, 120, 150, 180, 240$ and 300 min to determine spore survival. Additionally, measurements of H_2O_2 concentration, total iron (Fe^T) were determined at time 0, 120 and 300 min using the procedures described below. All the experiments were conducted in triplicate along with a negative control, the latter using 200 mL of sterile distilled water and *F. solani* at the same concentration described earlier but without the addition of any reagent, this reaction is known as solar disinfection (SODIS). The significance of the differences of survival curves of *F. solani* was determined by means of ANOVA using Minitab V.14®.

Experiments were performed from 10:30 to 15:30 (5 h) local time, in an open area exposed to direct sunlight. Solar radiation reaching the photoreactor was measured using a global UV-A radiometer (295–385 nm, Model CUV3, Kipp & Zonen, Netherlands) with a typical sensitivity of 264 mV/(W m^{-2}), placed at the same angle as the solar collector in order to avoid angle adjustments. The radiometer provides data in terms of incident radiation (W m^{-2}), which is defined as the solar radiant energy rate incident on a surface per unit area. A solar energy unit, Q_{UV}, is a term commonly used to compare results under different solar irradiation conditions (Goslich et al., 1997). Q_{UV} estimates the accumulated UV energy in the photoreactor per volume unit of treated water in a given time during the experiment. This factor allows researchers to normalize the energy available for the photocatalytic reaction under natural sunlight. Accumulated energy, defined as the total amount of irradiative energy reaching the reactor from the beginning of the experiment up to a given time by volume unit, was determined using the relationship previously reported by Polo-López et al. (2012):

$$Q_{UV} = Q_{n-1} + \Delta t G_n (A/V), \quad \Delta t = t_n - t_{n-1} \tag{1}$$

where Δt is the time between radiation measurements, Q_{UV} is the UV accumulated energy (kJ L^{-1}), G_n the global radiation (W m^{-2}) measured by the radiometer in each experiment, A the module area (m^2), and V the total system volume (L).

2.4. Analytical procedures

F. solani viability assessment was performed by taking 1 mL of sample. From this, 50, 250, or 500 μL were plated in malt agar (Sigma-Aldrich, USA) by plate extension technique, by duplicate. The plates were incubated at 28 °C for 48 h. After this time, spore concentration was determined by direct counting. The detection limit (DL) of the methodology was found 2 CFU mL^{-1}.

2.5. Iron concentration

For Fe^{2+} and total iron (Fe^T) evaluation, 4 mL of the sample were taken and mixed with 1 mL of 1,10-phenanthroline (1 g L^{-1}) (Merck, Germany) and 1 mL of buffer solution (ammonium acetate (Sigma-Alrdrich, UK) and acetic acid (J.T. Baker, Netherlands) according to ISO 6332 (1988). Then, the colored complex formed was measured using a spectrophotometer (PG Instruments Ltd T-60-U) at 510 nm in glass cuvettes (1 cm path length). Fe^{2+} and Fe^T concentrations were determined using the corresponding calibration curves.

2.6. H_2O_2 concentration

Hydrogen peroxide concentration was measured using 5 mL of sample in a spectrophotometer (PG Instruments Ltd T-60-U) at 410 nm in glass cuvettes (1 cm path length) according to DIN 38409 H15 (1987) based on the formation of a yellow complex from the reaction of titanium (IV) oxysulfate with H_2O_2. The titanium (IV) oxysulfate method has a 0.1 mg L^{-1} detection limit. The signal was measured after a five minute incubation time against a H_2O_2 standard curve linear in the 0.1–100 mg L^{-1} H_2O_2 concentration range as previously reported by Polo-López et al. (2012).

2.7. Modeling mold response

In order to perform a better analysis and evaluation of the results obtained for mold inactivation using the different

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