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Solar photo-Fenton for water disinfection: An investigation of the competitive role of model organic matter for oxidative species

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ABSTRACT

The competitive effect for the oxidative species produced during solar photo-Fenton process at neutral pH between an organic compound (resorcinol) and a model microorganism (*Enterococcus faecalis*) was investigated. With this purpose, the inactivation of *E. faecalis* was evaluated under several solar processes, i.e. SODIS, solar-UVA with H_2O_2 (10, 20 and 50 mg L^{-1}) and solar-UVA-Fe^{2+} (2.5, 5 and 20 mg L^{-1}) in the absence and presence of resorcinol (10 mg L^{-1}). The effect of resorcinol on the Fenton reaction (H_2O_2/Fe^{2+} in the dark: 5/2.5 and 50/20 mg L^{-1}) efficacy at neutral pH was also evaluated. In spite of resorcinol maintained a high amount of iron (around 10 mg L^{-1}) in solution during the experiments, with the highest concentrations of H_2O_2/Fe^{2+} (50/20 mg L^{-1}), only a 2-log decrease of bacteria was observed with 10 mg L^{-1} of resorcinol, while a 3.5-log abatement was detected without resorcinol. These results highlight the competitive role of organic matter for the oxidant species against bacteria when photo-oxidation and photo-disinfection processes are occurring at the same time. This competition for the oxidant species, mainly hydroxyl radicals generated during photo-Fenton, was confirmed by (i) the solar photo-Fenton assays at three different concentrations (H_2O_2/Fe^{2+}): 5/2.5, 10/5 and 20/10 mg L^{-1}, although at elevated concentrations of H_2O_2 and Fe^{2+} (50/20 mg L^{-1}) the disinfection efficiency was independent of the addition of resorcinol because an excess of radicals were generated, and (ii) by the photo-Fenton results obtained when the concentration of resorcinol was increased from 20, 30 till 40 mg L^{-1}.

1. Introduction

Water scarcity and groundwater contamination are serious problems since they affect to the human health. For these reasons, it is necessary to utilize treatments to ensure the water disinfection and reuse [1]. During wastewater treatment, the microbiological assessment of the water quality is usually carried out through the measurement of indicator microorganisms' concentration. *Escherichia coli* is the most commonly indicator of faecal contamination studied in wastewater disinfection. Parallel to the work on coliforms, a group of Gram-positive coccid bacteria known as faecal streptococci (FS) were being investigated as important pollution indicator bacteria [2]. Of the faecal streptococci, the preferred indicators of faecal pollution are the enterococci. The predominant intestinal enterococci are *Enterococcus faecalis*. Four key points in favour of the faecal streptococci were: (1) relatively high numbers in the excreta of humans and other warmblooded animals; (2) presence in wastewaters and polluted waters; (3) absence from pure waters, virgin soils and environments having no contact with human and animal life; (4) persistence without multiplication in the environment. Thus, according to the WHO guidelines on water quality, standards and health (2001), for water examination purposes enterococci, and particularly *E. faecalis*, can be regarded as indicators of faecal pollution of the water. Even, some authors have recently investigated on *E. faecalis* inactivation extrapolating their results for this model microorganism to bacterial consortia from wastewater treatment plant [3–5].

Recent studies propose the use of advanced oxidation processes (AOP) as alternative water disinfection technique. In particular, photo-Fenton may be used to efficiently treat wastewater contaminated with chemical pollutants [6,7] or pathogen microorganisms as bacteria, fungi, virus, etc. [8,9]. During the Fenton reaction, the hydrogen peroxide rapidly reacts with iron, and generates

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hydroxyl radicals, which are non-selective and highly oxidative species [10]. Iron is added at the beginning of the process and acts as a catalyst, being oxidized (Eq. (1)) and reduced continuously. Moreover, the presence of photons with wavelengths below around 550 nm (photo-Fenton system) leads to the generation of more hydroxyl radicals and regenerate Fe^{2+} (Eq. (2)) [10],

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + HO^- + HO^\bullet \quad (1)$$

$$[Fe(H_2O)]^{3+} + h\nu \rightarrow Fe^{2+} + HO^\bullet + HO^+ \quad (2)$$

The optimal pH of this process is 2.8, being much less efficient at near neutral pH due to the low solubility of iron salts at this pH. Hence, some authors are carrying out new research to overcome this problem. Some researchers have used specific systems to immobilize the iron. Cho et al. [11] employed a photo-ferrioxalate disinfection system (UV–visible light ions and oxalate), which allowed to obtain dissolved Fe^{3+} necessary for *E. coli* inactivation at neutral pH. Also, a woven inorganic silica fabric with Fe ions into (EGF-Fe) was checked in the inactivation of *E. coli K12* by photo-Fenton [12]. One of the most studied options consists of using different iron complexing as ethylenediamine-N,N′-disuccinic acid (EDDS) [13]. Klamerth et al. [13] showed that iron complexation with EDDS leads to stabilization and solubilization of Fe at natural pH although bacteria disinfection was not complete. Spluher et al. [14] reported that resorcinol, as a model of natural organic matter (NOM) present in the wastewater, improved the solubility of iron during the photo-Fenton process. Resorcinol and its degradation intermediates formed complexes with iron which were photoactive at neutral pH. The generation of reactive oxygen species was favoured leading to inactivation times for *E. coli* lower than when resorcinol was not present in the water [14].

However, the main challenge to disinfect wastewater containing organic matter is to achieve both chemical detoxification and microbial inactivation at the same time during the photocatalytic treatment. The presence of organic substances naturally present in water like dihydroxybenzenes isomers (resorcinol among others) showed a negative effect on photocatalytic disinfection of *E. coli* with TiO_2 [15]. Cho et al. [11] performed the inactivation of *E. coli* by TiO_2 in the presence of methanol as hydroxyl radical scavenger. Their results showed that methanol significantly inhibited *E. coli* inactivation (inactivation lower than 0.5-log in 60 min). Marugán et al. [16] studied the TiO_2 photocatalytic treatment for methylene blue chemical oxidation and *E. coli* inactivation. They concluded that changes in the activity for the oxidation of the organic molecule cannot be extrapolated to the photocatalytic disinfection processes. However, observations of Chen et al. [17] indicated that there was an apparent correlation between the two photocatalytic processes of decomposing formaldehyde and inactivating *E. coli* for TiO_2 treatment.

The aim of this research was to study the role of an organic molecule as resorcinol (considered as a model of NOM) on the disinfection process by solar photo-Fenton at neutral pH; so that the accelerating or competitive effect of this organic matter was discriminated. A deep study on the variables involved, i.e. reagents dosage and concentration of organic compound was performed. With this purpose, inactivation of *E. faecalis* was investigated by solar disinfection (SODIS), UVA-H_2O_2, UVA-Fe^{2+} and Fenton reaction. *E. faecalis* disinfection by solar photo-Fenton was evaluated with four initial concentrations of H_2O_2 and Fe^{2+}. The concentration of resorcinol in all assays was 10 mg L^{-1}. Finally, the *E. faecalis* inactivation by photo-Fenton was also evaluated with higher concentrations of resorcinol. Experiments without resorcinol were included in all experiments as reference.

2. Materials and methods

2.1. Bacterial strain and inoculum preparation

E. faecalis CECT 5143 was acquired from the Spanish Culture Type Collection (Colección Española de Cultivos Tipo, Valencia, Spain). Cultures of *E. faecalis* were grown in Streptococcus Selective Broth media (Biolife) and incubated at 37 °C with constant agitation in an orbital shaker at 150 rpm for 24 h. *E. faecalis* was harvested in stationary phase by centrifugation at 3000 rpm for 10 min and washed three times with saline solution (0.9% NaCl) obtaining a final bacterial concentration of 10^6 CFU mL^{-1} (determined by optical density at 600 nm). The required stock volume was added to saline solution in order to avoid osmotic stress and its resultant detrimental effect on cell viability during the experiments. Saline solution was prepared with sterile Milli-Q water.

2.2. Experimental procedure

Inactivation of *E. faecalis* was investigated using the following solar promoted processes: (i) solar disinfection ($SODIS_{[0]}$); (ii) solar UVA with added H_2O_2 at 10, 20 and 50 mg L^{-1}; (iii) solar UVA-Fe^{2+} (2.5, 5 and 20 mg L^{-1}); and (iv) Fenton reaction at two concentrations of reagents H_2O_2/Fe^{2+}: 5/2.5 and 50/20 mg L^{-1}; (v) *E. faecalis* disinfection by solar photo-Fenton was evaluated at four different concentrations of hydrogen peroxide and iron (H_2O_2/Fe^{2+}): 5/2.5, 10/5, 20/10 and 50/20 mg L^{-1}. Resorcinol was present at same concentration, 10 mg L^{-1}. Finally, other photo-Fenton tests were also carried out at higher concentrations of 20, 30, and 40 mg L^{-1}. As a reference, photo-Fenton experiments were also done without resorcinol. The experiments were done in triplicate, the results did not show significant statistical variations (the confidence level was greater than 95%).

All experiments were carried out in 250 mL Duran-Glass (Schott, Germany) stirred tank reactors under natural sunlight. Glass covers were used to allow the solar radiation to enter the reactor from all directions. The reactors were stirred at 150 rpm during the experiment. The UVA radiation and temperature was measured online during the experiments with a radiometer (Delta OHM LP UVA 02 model) and with a probe (Crison 60 50), respectively. Data were obtained by a data acquisition card (LabJack U12) connected to a computer. Mean temperature and UVA radiation values were 28 ± 1 °C and 30 ± 2 W m^{-2}, respectively.

For all experiments, prior to bacterial spiking, a control sample was taken to check the non-presence of any other microorganisms in the Milli-Q water. Bacterial suspension was mixed for 2 min in the dark and a second control sample was taken. This control was kept in the lab (in the dark, at room temperature) and plated at the start and end of the experiment to check cell viability without undergoing any of the treatments. The samples taken during the experiments were enumerated using the standard plate counting method through 10-fold serial dilutions in Streptococcus Selective Broth (Biolife, Italy) (30.6 g L^{-1}) and agar (15 g L^{-1}). A volume of 20 μL was plated three times for each one of the four 1:10 dilution. Colonies were counted after 24 h incubation at 37 °C. The detection limit was 1 CFU mL^{-1}. This procedure was carried out in triplicate for each sample. In order to test cell recovery post-treatment, the samples were maintained in the dark after the treatment for predetermined exposure times. These samples were plated for colony counting after a 24 h period.

2.3. Analytical determinations

Ferrous sulfate heptahydrate ($FeSO_4 \cdot 7H_2O$ >99%, Fluka, Spain) was used as a source of Fe^{2+}. Iron concentration was analyzed by the o-phenantroline standardized method according to ISO 6332.