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Wild bacteria inactivation in WWTP secondary effluents by solar photo-fenton at neutral pH in raceway pond reactors

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ABSTRACT

For first time, the efficiency of raceway pond reactors for wastewater disinfection by solar photo-Fenton (50 mg H_2O_2/L and 20 mg Fe^{2+}/L) at neutral pH has been shown in this study. Complete inactivation of wild total coliforms, *E. coli* and *Enterococcus* sp. in municipal wastewater treatment plant secondary effluents took place after 80 min. A comparison with a tubular reactor equipped with a compound parabolic collector (CPC) was carried out and disinfection times were the same for the CPC and RPR, the tubular one having a 5 cm tube diameter and the RPR was operated at 5 cm liquid depth. Both acute and chronic toxicity were evaluated before and after treatment in both reactors and their analysis showed no significant changes for the removal of either in the treated effluent in both reactors. Additionally, an economic assessment of the process in the RPR was also performed. Estimated total costs for a 400 m^3/d scale solar photo-Fenton plant for disinfection (0.15 €/m^3) were in the range of reclaimed water rates.

1. Introduction

In a scenario of water-scarcity, wastewater reuse appears to be one of the most attractive options to develop non-conventional water resources, agricultural irrigation being the most established application [1]. Despite wastewater reuse being able to provide important economic benefits by reducing wastewater disposal and irrigation costs, some public health and environmental concerns must be addressed for safe and rational implementation of wastewater reuse in agricultural settings [2]. In this regard, to minimize health risks, the control of pathogenic microorganisms are among the most common parameters set in water quality standards for agriculture [3–5].

The use of disinfectants such as chlorine is still the most widely applied disinfection method to inactivate pathogenic microorganisms in wastewater. Nonetheless, the generation of undesirable disinfection by-products, some of them categorized as potential human carcinogens, has forced the scientific community to explore alternative disinfection methods such as advanced oxidation processes (AOPs) [6]. Amongst them, solar driven processes (heterogeneous and homogeneous photocatalysis) which can take advantage of natural sunlight, thereby lowering treatment costs, have received great attention [7–9]

Although both solar photo-Fenton and heterogeneous catalysis with TiO_2 have proved to be efficient for real municipal wastewater disinfection, the removal of the catalyst (TiO_2) after treatment is still considered a drawback for its application in terms of wastewater reuse [8]. Regarding photo-Fenton, even though the process is more efficient at acidic pH, research has been directed towards extending the process at neutral pH to avoid the operating costs associated with acidification and subsequent neutralization [10]. In this regard, the capability of photo-Fenton process for real wastewater disinfection attaining the quality standards for water reuse, have been recently demonstrated [11].

However, up to now there are no solar photo-Fenton demo plants for disinfection at large scale. One of the main shortcomings involving with scaling-up the process is the cost, where that of investment, namely for the photoreactor, plays an important role. Compound parabolic collectors (CPCs) are the most popular photoreactors used for microorganism inactivation and pollutant degradation due to their successful exploitation of solar photons [12]. Nevertheless, the cost for the installation of a large scale CPC for solar photo-Fenton was estimated at 400 €/m^2 [13]. Thus, to bring the application of this solar treatment closer to industrial scale, the use of low cost reactors such as raceway pond reactors (RPRs) with low construction costs (around 10 €/m^2) could be a more viable option.

Several studies have demonstrated the successful application of RPRs, with less efficient optics but a larger treated volume/surface ratio than for CPCs, regarding micropollutant and related toxicity removal [14,15]. However, very little is known about the application of solar

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photo-Fenton at neutral pH for wastewater disinfection in RPRs.

In light of these facts, this work was aimed at studying the feasibility of RPRs for disinfection of secondary effluents by the solar photo-Fenton process at neutral pH. For this purpose, the most favorable conditions (20 mg Fe/L and 50 mg H_2O_2 mg/L) reported in a CPC pilot plant to disinfect real wastewater by solar photo-Fenton at neutral pH [11] were simultaneously tested in a 5 cm-deep RPR and in a tubular CPC with 5 cm tube diameter. The concentrations of total coliforms (TC), *Escherichia coli (E. coli)* and *Enterococcus* sp. were monitored as fecal contamination models in wastewater since these organisms represent a wide number of pathogenic bacteria. A toxicological analysis was carried out before and after the treatment in each photo-reactor, while an economic assessment was also performed.

2. Materials and methods

2.1. Water matrix

Experiments were performed with effluents collected from the "El Bobar", the municipal wastewater treatment plant (MWWTP) located in Almería (Southern Spain). This plant treats the wastewater from a population equivalent to 100000 and generates 11.6 hm^3 of secondary effluent yearly through conventional activated sludge and decantation. The characterization of the secondary effluent used during the experimentation is shown in Table 1.

2.2. Solar photo-reactors

Solar photo-Fenton experiments were carried out at pilot scale using two types of reactors: CPCs and RPRs.

The CPC pilot plant consisted of two twin 7 L reactors made of Pyrex tubes (1.5 m length and 5 cm diameter), the illuminated volume being 2.1 L [16]. Two twin RPRs with 5 cm liquid depth and maximum working volume of 18 L were used. They were made of PVC with 0.98 m in length and 0.37 m in width forming two channels [13]. The ratio illuminated to total volume in CPC was 0.3 due to the presence of dark zones (mainly the recirculation tank) whereas the RPR was completely illuminated as it is an open reactor. Mixing time in the CPC reactors was 5 min and 3 min in the RPRs.

All plants were equipped with temperature (Crison 60 50) and pH (Crison 53 35) probes. UVA radiation (global UV radiometer Delta Ohm, LP UVA 02 AV), pH and temperature were monitored on-line using a LabJack U12 data acquisition card connected to a computer. Two radiometers were used to measure the irradiance reaching each photo-reactor, one tilted 37° facing south for the CPC and another horizontally placed for the RPR.

Table 1
Physical-chemical and microbiological characterization of secondary effluent batches from MWWTP.

Parameter	Average ± Standard Deviation (n = 40)
pH	7.7 ± 0.2
Conductivity (mS/cm)	1.2 ± 0.2
Turbidity (NTU)	7.4 ± 2
Dissolved Organic Carbon, (DOC; mg/L)	18.9 ± 5.1
Total Inorganic Carbon, (TIC; mg/L)	80 ± 8.1
Chemical Oxygen Demand, (COD; mg/L)	65.1 ± 1.4
Bicarbonates (mg/L)	408.5 ± 40.5
Phosphate (mg/L)	5.8 ± 0.5
Chloride (mg/L)	446.8 ± 15.4
Bromide (mg/L)	3.1 ± 0.2
Sulfide (mg/L)	127.0 ± 23.6
Nitrate (mg/L)	48.4 ± 6.5
Nitrite (mg/L)	2.7 ± 0.03
TC (CFU/mL)	$3.54{\cdot}10^6 \pm 1.7{\cdot}10^5$
E. coli (CFU mL/L)	$2.76{\cdot}10^4 \pm 3.1{\cdot}10^2$
Enterococcus sp (CFU/mL)	$7.1{\cdot}10^3 \pm 1.5{\cdot}10^1$

2.3. Experimental procedure

For comparison purposes, experiments were carried out simultaneously in the CPC and RPR at neutral pH. All assays were performed with the MWWTP effluent pre-treated with sulfuric acid 2 N setting pH at 7.0 ± 0.2 to reduce total inorganic carbon concentration, TIC, until a final value of 50 ± 11 mg TIC/L and partially avoid the scavenger effect of bicarbonates (measured as TIC). Once the pilot plants were filled with the MWWTP secondary effluent and covered, 50 mg H_2O_2/L was added to each reactor. The liquid was mixed by recirculation for several mixing times in each photo-reactor. After that, the iron salt (20 mg Fe^{2+}/L) was added and the reactors were promptly uncovered starting the reaction.

Experiments were performed in triplicate on different days to take into account the variability of the wastewater and in duplicate every day using twin photo-reactors. All assays were started at noon to ensure an almost constant value of solar irradiance and water temperature. The average irradiance and temperature were 35 ± 1.3 W/m^2 and 34 ± 2.1 °C for the CPC and 30 ± 2 W/m^2 and 27 ± 3.0 °C in the RPR.

2.4. Control experiments

Control experiments were performed simultaneously in CPC and RPR under the following conditions: i) in the dark without any reagent to check the effect of the mechanical stress at the flow conditions set for each photo-reactor, ii) in the presence of sunlight (UVA), iii) with hydrogen peroxide (UVA/H_2O_2), iv) with iron in the dark (Fe) and with sunlight (Fe/UVA), and the Fenton reaction (50 mg H_2O_2/L and 20 mg Fe/L).

2.5. Bacterial enumeration

The wild enteric bacteria concentrations (TC, *E. coli* and *Enterococcus* sp.) in the MWWTP effluent were evaluated using standard plate counting methods [11,16]. This procedure was carried out in triplicate for each sample and the detection limit (DL) was 1 CFU/mL for the three species. The initial TC concentration ranged from 10^6 to 10^5, *E. coli* varied in the range 10^4–10^2 and *Enterococcus* sp. from 10^3 to 10^1. In order to evaluate cell recovery after treatment, final samples were maintained in the dark for two days at room temperature. Then the samples were plated and incubated at 37 °C for 1 day for colony counting. No regrowth was detected.

2.6. Kinetic evaluation

The inactivated bacteria population was fitted to first order kinetics according to Chick's law, Eq. (1),

$$\log(C/C_0) = -kt \quad (1)$$

where C/C_0 is the organism concentration reduction, k represents the rate constant (1/min) of bacteria inactivation and t is the treatment time (min).

2.7. Chemical and analytical determinations

Before chemical analysis, all samples were filtered with 0.2 µm syringe-driven filters (Millex®, Millipore). Ferrous sulfate heptahydrate ($FeSO_4{\cdot}7H_2O$, 99%, Panreac) was used as a source of ferrous iron. The concentration of iron was determined by the o-phenantroline standardized method (ISO 6332). Hydrogen peroxide (33%, w/v aqueous solution, Panreac) concentration was analyzed by a colorimetric method (DIN 38409–15) using titanium (IV) oxysulftate (98%, Sigma-Aldrich,