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Disinfection of real and simulated urban wastewater effluents using a mild solar photo-Fenton

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ABSTRACT

This work aims to assess the effectiveness of a mild solar photo-Fenton system (low reagent concentrations and near neutral pH) for the removal of fecal bacteria in urban wastewater effluents. *Escherichia coli* and *Enterococcus faecalis* were simultaneously evaluated in real and simulated effluents at initial concentrations of 10^3 and 10^6 CFU/mL. Several concentrations of ferrous sulfate (2.5–10 mg-Fe^{2+}/L) and hydrogen peroxide (5–50 mg/L) were tested in solar CPC reactors (total volume: 20 L) under natural sunlight. Photo-Fenton results were compared with the bactericidal effects of solar exposure and H_2O_2 under the same experimental conditions. Solar photo-Fenton processes at pH 5 and pH 3 were compared. The results showed complete bacterial inactivation in almost all conditions, but the solar UVA energy dose required to achieve similar results at pH 5 (24–30 kJ/L) was higher than at pH 3 (2–20 kJ/L). This work also shows experimentally that the presence of precipitated iron at near-neutral pH has no benefits for disinfection efficacy; it actually causes a slight decrease in effectiveness under these experimental conditions. *E. faecalis* clearly showed higher resistance than *E. coli* to all treatments (photo-Fenton and H_2O_2/solar) using both naturally occurring and seeded bacteria. The disinfection tests in real effluents showed very promising results despite the complexity and variability of the organic and inorganic matter in the effluents. A 3-log decrease in *E. coli* and *E. faecalis* was attained in real effluents, and a 6-log abatement was observed in simulated wastewater when the solar photo-Fenton process at pH 5 was used. This result has important implications for the treatment of reclaimed wastewater.

1. Introduction

The growth of the world population is accompanied by an increase in industrial, agricultural and recreational activities. These activities, in turn, increase the demand for fresh water. For this reason, in the next few decades, access to clean fresh water sources will be a serious global problem. Water scarcity and the health risks associated with polluted water resources will be major global issues.

The primary purpose of the reclamation and reuse of water is to draw water directly from non-traditional sources, such as industrial or municipal wastewaters, and to restore it to higher quality [1]. Wastewater contains a great diversity of chemical pollutants and pathogens, and it includes a large amount of organic matter, all of which must be removed or transformed into harmless compounds.

Wastewater reuse may provide a new and stable source of water for agriculture, industrial processes, and some domestic uses that do not require potable water. The potential benefits for agriculture, environmental preservation, and energy conservation may be even more important.

The agricultural sector is the largest consumer of fresh water, using 70–95% of it for irrigation. Wastewater reuse in agriculture will reduce stress on the water supplies in semi-arid and very contaminated areas [2]. Guidelines and specific national policies for reclaimed water quality and reuse limit the loads of several waterborne pathogens, such as fecal coliforms and *Escherichia coli* [3–7]. Depending on the final use of the reclaimed water, the maximum allowed concentrations of microbial agents vary; they are more restrictive for urban and agricultural uses and less restrictive for industrial, recreational, and environmental uses. In particular, the guidelines for water recycling, established by different water authorities for unrestricted irrigation, are as follows for *E. coli* and coliforms, in terms of CFU per 100 mL: <1 as defined by the USEPA [3], <1000 as defined by the WHO [4], <10 as defined by Italian rules [5], <1 as defined by Australian guidelines [6] and <100 as defined by Spanish regulations [7].

Urban wastewaters are commonly treated with activated sludge, followed by treatment in sedimentation systems (secondary treatment). Depending on the regulations in each area or

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country, these wastewater effluents may be able to be discharged to surface waters or used for restricted irrigation and industrial applications. Based on the microbial quality requirements established by various agencies, it is clear that an efficient tertiary treatment of effluents is needed.

Mostly, urban wastewater effluents contain, among other pollutans, high loads of fecal bacteria. Levels of these bacteria are commonly reported in terms of the concentrations of *E. coli*, total coliforms (TC) and fecal coliforms (FC). *E. coli* normally accounts for the majority of the fecal coliform group [8]. The typical quality of these wastewater effluents is approximately 10^3–10^5 TC/100 mL [9–11]. The fecal load limit established by the WHO for unrestricted irrigation uses is ≤1000 CFU of FC/100 mL [4].

Different physicochemical water treatments are currently in use, including treatments with chlorine, UVC, and ozone. Although chlorine is a very strong oxidant and has a residual effect, it may react with natural organic matter (NOM) to form carcinogenic halogenated disinfection by-products (DBP), such as trihalomethanes (THMs) and haloacetic acids (HAA) [12–14]. The use of UVC has limited efficiency against very resistant pathogens [15], it has a non-residual effect, and it requires high capital costs and high operation and maintenance costs. Thus, alternative technologies are being studied for the removal of water pathogens to overcome these limitations. Some advanced oxidation processes (AOPs), such as H_2O_2/UV-C, photocatalysis with titanium dioxide, photo-Fenton processes and H_2O_2/O_3, are being proposed as new approaches for water disinfection [16–22]. The efficacy of AOPs lies in the generation of hydroxyl radicals ($OH^\bullet$). These highly oxidating species can oxidize almost all organic compounds and can inactivate a wide range of microorganisms. Furthermore, the use of solar radiation to promote some AOPs has been demonstrated to be very efficient for water purification, and it has the advantage of relying on an environmentally friendly source of photons [23].

Recently, research has been conducted on mild photo-Fenton and solar radiation with low concentrations of H_2O_2 for water disinfection [21,24]. Photo-Fenton produces hydroxyl radicals via a series of catalytic cycle reactions with iron (Fe^{2+} and Fe^{3+}), H_2O_2 and UV–vis radiation (≤600 nm). These reactions are summarized as follows [25]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + OH^\bullet \quad (K = 70\,M^{-1}\,s^{-1}) \tag{1}$$

$$Fe(OH)^{2+} + h\nu \rightarrow Fe^{2+} + OH^\bullet \tag{2}$$

The highest photo-Fenton efficacy is found at pH 2.8 [25] because this pH minimizes the precipitation of iron salts. Nevertheless, photo-Fenton reactions at near-neutral pH values would be desirable to reduce operational costs associated with acidification and neutralization of large volumes of wastewater. Few articles have dealt with this subject [21,26,27]. These papers have reported the successful inactivation of single bacteria (*E. coli* or *Enterococcus faecalis*) in different water matrixes under very different conditions. There is still scarce information about the applicability of this process for the disinfection of real wastewaters under realistic solar conditions.

Solar photo-assisted treatment with H_2O_2 induces accelerated inactivation of several types of microorganisms in water due to photo-chemical and photo-biological processes that occur when solar photons and non-toxic amounts of hydrogen peroxide interact with living cells [20,28,29]. This phenomenon cannot be considered to correspond to any of the well-known AOPs because it does not generate hydroxyl radicals by the photo-chemical reaction of H_2O_2 with sunlight (wavelengths >300 nm) [30]. Our previous research on H_2O_2/sunlight processes for water decontamination has shown that no significant degradation of organic matter occurs during disinfection [24]. It is believed that the mechanism of action of this method is based on the stressing effect produced by H_2O_2 and solar photons due to internal photo-Fenton reactions with the available iron inside the microbial cells [31].

The efficiency of water disinfection strongly depends on water composition and the inhabiting bacterial consortium. The role of organic matter is controversial; some articles report that it provides a beneficial effect for disinfection, and others report that it is detrimental [21,24,27,32]. There are few reports on the removal of bacterial consortia and naturally occurring bacteria in real wastewaters [29,33] using photo-Fenton treatment or H_2O_2/solar treatment.

The aim of this work was to evaluate the efficiency of a solar photo-Fenton process at near neutral pH and a H_2O_2/solar process for removing *E. coli* K-12 and *E. faecalis* simultaneously spiked into simulated municipal wastewater effluents and naturally occurring *E. coli* and *E. faecalis* in real municipal wastewater effluents. Several concentrations of ferrous sulfate (2.5–10 mg-Fe^{2+}/L) and hydrogen peroxide (5–50 mg/L) were evaluated in two solar CPC reactors under natural solar conditions. The effect of pH on solar treatment efficiency was evaluated at pH 3 and pH 5. Furthermore, the influence of precipitated and dissolved iron on the efficiency of the photo-Fenton process at near-neutral pH values was also investigated. A pH level of 7 was not experimentally evaluated, as our previous publications [24,33] showed that the inactivation of *E. coli* and *Fusarium solani* spores by a photo-Fenton process at pH 7 were very similar to those observed for an H_2O_2/solar process. This result was attributed to the fact that no dissolved iron was measured in the samples at this pH.

2. Materials and methods

2.1. Solar experiments

All experiments were conducted at Plataforma Solar de Almeria (PSA) under natural solar radiation on completely sunny days, from April to July 2012 (summer conditions), for 4 h of solar exposure (10:30–14:30, local time).

Three types of solar experiments were performed in this work: (i) H_2O_2/solar treatment and (ii) solar photo-Fenton treatment. Both treatments were performed in simulated effluents (SE) and real effluents (RE) from urban wastewater treatment plants using CPC pilot reactors. (iii) Solar photo-Fenton experiments were conducted to study the effect of the presence or absence of precipitated iron in small stirred vessel reactors in distilled water (DW).

2.1.1. Solar CPC pilot reactors

Most of the experiments were performed in two pilot plants equipped with compound parabolic collector (CPC) reactors (Fig. 1). Both reactors are recirculated batch systems with total volumes of 20 L and illuminated volumes of 14 L in the CPC photo-reactors. The ratio of illuminated volume to total volume is 0.7. The CPC mirrors (total surface area of 1 m^2) are titled at an angle of 37° relative to the horizontal plane, which enhances the solar radiation collection [34]. The flow rate was 10 L/min in both reactors.

The experiments were performed in SE and RE. Water was acidified using sulfuric acid (Merck, Germany, analytical grade) after adding iron salts in the photo-Fenton experiments. Then, the bacterial suspensions were added to the SE, and, finally, the hydrogen peroxide was added. The same procedure was followed in the RE samples, without spiking the bacteria because the naturally occurring *E. coli* and *E. faecalis* were evaluated in those samples.

Samples were taken at predetermined times for a period of 4 h. The ‘dark control sample’ was the first sample of each experiment kept in the dark at room temperature, which was analyzed at the end of the experiment to examine the effects of the process in the dark on bacteria viability. Temperature (T) (Checktemp, Hanna