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Modelling of the operation of raceway pond reactors for micropollutant removal by solar photo-Fenton as a function of photon absorption

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ABSTRACT

Raceway ponds reactors (RPRs) are extensive non-concentrating photoreactors which allow large volumes of water to be treated. They consist of channels where water is set in motion by a paddlewheel system. In this work the effect of solar irradiance on RPR operation to remove micropollutants by solar photo-Fenton was studied. A RPR was used at pilot plant scale (up to 360 L) and the pesticides acetamiprid (ACTM) and thiabendazole (TBZ) were used as a model pollutant mixture (100 μg/L each) in simulated effluent. Averaged UV irradiances ranged from 10 to 30 W/m^2 and three values of iron concentration (1, 5.5 and 10 mg/L) were used. Different liquid depths were also used to evaluate the relationship between the rate of photon absorption and pollutant removal. A model was proposed to predict degradation rate and treatment capacity as a function of the volumetric rate of photon absorption (VRPA). Under low irradiance conditions (10 W/m^2) the treatment capacity was not sensitive above 10 cm liquid depth, so a low iron concentration should be used (5 mg Fe/L). For high irradiance values (30 W/m^2), greater liquid depth (20 cm) and iron concentration (10 mg Fe/L) should be used to take full advantage of photon availability. Treatment capacity values of 133 mg/h m^2 can be reached under these conditions.

1. Introduction

There is an increasing environmental concern about organic contaminants found in waters at concentrations in the ng/L–μg/L range, named micropollutant [1–4]. They cover a great variety of organic compounds such as pharmaceuticals, personal care products and pesticides. They are released to wastewater effluents by anthropogenic activities, reaching wastewater treatment plants (WWTPs). However, conventional methods such as biological treatments are not enough to remove these compounds [5]. As a result, micropollutants continuously escape into the environment [6–8]. They can pose potential environmental risks. For instance, phenomena such as bioaccumulation or hermaphroditism in fish have been reported in recent years due to DNA alterations by endocrine disruptors [9,10]. Consequently, research is being developed to remove them by including a tertiary stage in WWTPs. In this regard, advanced oxidation processes (AOPs) have been widely used due to their efficiency in recalcitrant pollutant mineralisation to CO_2 and H_2O [11]. They are based on the generation of oxidative radicals which oxidise organic compounds. Amongst them, the photo-Fenton process has proved to be effective in micropollutant removal [12]. Specifically, this process is based on the redox iron cycle to generate hydroxyl radicals ($HO^\bullet$) ($E_0 = -2.8$ V). In summary, iron acts as catalyst and is oxidised and reduced cyclically: ferrous iron (Fe^{2+}) reacts with hydrogen peroxide, yielding hydroxyl radicals and is oxidised to ferric iron. Subsequently, ferric iron can absorb light in the UV–vis range, also yielding hydroxyl radicals and reducing it to ferrous iron again. Consequently, this process is strongly dependent on iron concentration and irradiance and both are important factors in reactor design and process operation [13,14].

The absorption of irradiance by the catalyst is greatly affected by light distribution inside the photoreactor and therefore has a direct influence on the process kinetics [15,16]. As such, photoreactor configuration is critical. To remove pollutants in the

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mg/L–g/L range (macropollutants), tubular compound parabolic collectors (CPCs) are the most optimised photoreactors for solar-driven photo-Fenton [17]. They make the most out of the beams reaching the reactor surface and allow generating high concentration of hydroxyl radicals working with solar irradiation. A drawback of this system though, is that they do not have a good efficiency when working with low concentration of contaminants needing low concentration of hydroxyl radicals as the ratio treated volume/surface is low. Photoreactor diameter (light path length) is in the range of a few cm for optimising costs of solar collector, glass tube and pressure drop and under these conditions optimal Fe concentration for maximising photons absorption is in the range of 0.2–0.3 mM [14]. Under these conditions, too high concentration of radicals would be produced for removing microcontaminants and therefore an important part of them would be wasted. Therefore, to remove pollutants in the μg/L–ng/L range (micropollutants) by solar-driven photo-Fenton, CPCs seems not to be the best choice.

Therefore, photoreactors with less efficient optics but a larger treated volume/surface ratio (i.e., longer light path length) could be used [18]. The light path length can be enlarged only by increasing the liquid depth in very simple photoreactors like solar ponds. In this way, raceway pond reactors (RPRs) could provide a good alternative for micropollutant degradation. They consist of open channels forming a raceway where the liquid is set in motion by a paddlewheel. They have been used for a long time for solar applications like microalgal mass culture [19] and are enough developed from an engineering point of view [20]. They allow wider optical paths (proportional to liquid depth in the photoreactor) than tubular photoreactors, so more volume can be treated per surface unit. Nevertheless, the appropriate optical path depends on liquid depth, iron concentration and irradiance distribution in the reactor. Indeed, liquid depth could be used as an operation variable and set as a function of solar irradiance.

This work was aimed at studying the effect of solar irradiance on RPR operation to remove micropollutants with solar photo-Fenton at pilot plant scale. For this purpose, a mixture of commercial pesticides, acetamiprid (ACTM) and thiabendazole (TBZ), 100 μg/L each, was used in simulated secondary effluent of municipal wastewater treatment plant (MWTP) as a model pollutant mixture, avoiding the disturbance of daily variations in real effluents. Both pesticides are commonly applied to citrus crops in the Mediterranean area. Outdoor experiments were carried out from February to May 2014, at two liquid depths, 5 cm and 15 cm, which corresponded to 120 L and 360 L water volume. Averaged UV irradiances ranged from 10 to 30 W/m^2. Three values of iron concentration (1, 5.5 and 10 mg/L) were used to study the relationship between the rate of photon absorption and pollutant removal.

2. Materials and methods

2.1. Chemicals

Sulphuric acid (95–97%) and hydrogen peroxide (35%) were obtained from J.T. Baker and ferrous sulphate (99%) from Fluka. $CaSO_4{\cdot}2H_2O$, $MgSO_4$, KCl, $(NH_4)_2SO_4$, $NaHCO_3$, beef extract, peptone, humic salts, sodium lignin sulfonate, sodium lauryle sulphate, acacia gum powder, formic acid and Arabic acid were acquired from Sigma–Aldrich. Commercial formulations of pesticides were used: EPIK® (20% (w/w) ACTM) and TEXTAR® (60% (w/v) TBZ). HPLC grade acetonitrile from Carlo Erba Reagents and Milli-Q grade water were used in the chromatographic analysis.

2.2. Experimental set-up

The experiments were carried out in a fibreglass-RPR pilot plant in the Centre for Solar Energy Research (CIESOL) in Almería, Spain. A

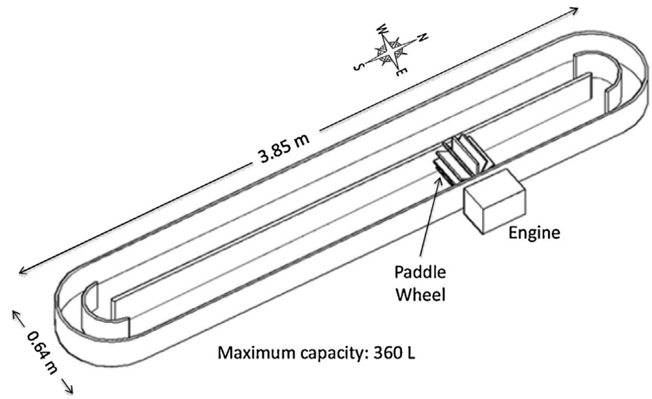

Fig. 1. RPR scheme.

pH value of 2.8 was chosen because it is the optimum for the photo-Fenton process [21] and allows a higher solubility of iron, allowing evaluating properly the efficiency of RPRs. Future work will be focused on working at circumneutral pH in RPRs, recommended to treat micropollutants [22]. The fibreglass-RPR has a maximum capacity of 360 L, a length of 3.85 m and width of 0.64 m. It is separated by a central wall, forming two channels. The RPR includes a paddlewheel connected to an engine to obtain a mixed and homogeneous flow during the process. The engine was linked to a variable frequency drive to control the paddles' speed. A scheme of the plant is presented in Fig. 1. The Reynolds number was estimated for each liquid height and a turbulent regime was used: 6×10^5 and 7×10^5 for 5 cm and 15 cm liquid depth, respectively.

Iron concentration and liquid depth (treated volume) were the process variables studied. Iron concentration was kept to low values, 1, 5.5 and 10 mg/L, typically used for micropollutant removal [12,23]. Low concentrations of iron contribute to prevent large generation of iron sludge when neutralising the effluent after the treatment. Initial hydrogen peroxide concentration was 50 mg/L to work in oxidant excess conditions. Liquid depth, which determines irradiance path length, was 5 cm and 15 cm. The first value was taken as the common diameter (light path length) used in tubular reactors of CPCs [16]. The last depth value is the maximum allowed by the configuration of the RPR reactor. As the liquid depth changes, so does the treated water volume in each case. To ensure similar mixing times the paddlewheel speed was changed according to the treated volume and mixing time was experimentally measured by means of a pulse test with a tracer. The result was a ∼2.5 min mixing time for all cases.

UV radiation was measured using a global UV radiometer (Delta Ohm, LP UVA 02 AV) with a spectral response range from 327 to 384 nm, mounted on a horizontal platform, providing data in terms of incident UV radiation (W/m^2). The experiments were run in the central hours of the day to have the minimum variation in solar radiation under stable weather conditions.

The plant was equipped with pH and temperature probes. The variables were monitored on-line by means of a LabJack USB/Ethernet data acquisition device connected to a computer. Prior to the beginning of the experiments, the reactor was covered and pH was adjusted to 2.8 ± 0.05 with sulphuric acid. A recirculation time of 5 min was allowed for homogenisation after the addition of the pesticide mixture and iron salt, corresponding to twice the mixing time in the photoreactor.

Both ACTM and TBZ are commonly used in citrus crops which predominate in the Mediterranean agriculture (e.g. lemon, orange trees) [24,25]. ACTM is a neonicotinoid insecticide and it has been reported to be more resistant to oxidation than other pollutants typically found in WWTP effluents [18,26]. TBZ is a widely used