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Sono-photo-degradation of carbamazepine in a thin falling film reactor: Operation costs in pilot plant

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ABSTRACT

The photo-Fenton degradation of carbamazepine (CBZ) assisted with ultrasound radiation (US/UV/H_2O_2/Fe) was tested in a lab thin film reactor allowing high TOC removals (89% in 35 min). The synergism between the UV process and the sonolytic one was quantified as 55.2%.

To test the applicability of this reactor for industrial purposes, the sono-photo-degradation of CBZ was also tested in a thin film pilot plant reactor and compared with a 28 L UV-C conventional pilot plant and with a solar Collector Parabolic Compound (CPC). At a pilot plant scale, a US/UV/H_2O_2/Fe process reaching 60% of mineralization would cost 2.1 and 3.8 €/m^3 for the conventional and thin film plant respectively. The use of ultrasound (US) produces an extra generation of hydroxyl radicals, thus increasing the mineralization rate.

In the solar process, electric consumption accounts for a maximum of 33% of total costs. Thus, for a TOC removal of 80%, the cost of this treatment is about 1.36 €/m^3. However, the efficiency of the solar installation decreases in cloudy days and cannot be used during night, so that a limited flow rate can be treated.

1. Introduction

Process intensification is about providing a chemical process with the precise environment required which results in better products, and processes which are safer, cleaner, smaller and cheaper [1]. Some features include moving from batch to continuous processing, using new emerging technologies (such as ultrasound) and use of intensive reactor technologies with high mixing and heat transfer rates in place of conventional stirred tanks [2,3].

Regarding the first feature, homogeneous advanced oxidation processes (AOPs) have been largely used to degrade refractory organic pollutants present in water [4–7]. Sonophotocatalysis (consisting of a combination of ultrasonic sound waves, ultraviolet radiation and a catalyst) has recently emerged as an alternative water treatment method [8–10] due to several advantages: lower doses of catalysts and reagents, no need for low turbidity, etc. However, the use of high-frequency ultrasound demands high amounts of energy, so that an economical study in needed to quantify its applicability in each reactor type.

A previous research [11] showed the important contribution of ·OH radicals during degradation of carbamazepine under the US-UV-H_2O_2-Fe system. Under optimum conditions, mineralization reached 93% in 35 min under batch conditions. The authors also performed a study of the flow pattern inside the reactor, showing that improvement in mineralization rate with US radiation could not be attributed to a positive effect in mixing. Thus, the aim of this research is focussed on i) understanding the effect of US radiation on the formation of hydroxyl radicals to improve mineralization, ii) to perform mineralization tests at a pilot plant scale and iii) to analyze the economic viability of the process.

Regarding the use of new reactor technologies and in addition to conventional batch reactors, in the last years several new type of reactors have been developed to remove pollutants from water effluents including thin film reactors and collector parabolic compound (CPC). Thin film reactors have a large heat and mass transfer area per unit liquid volume that make them very efficient in industry. They have low contact time, low pressure drop, and easy cleaning. The main inconvenience is that high flow rates induce waves in the falling liquid and the film can be broken. To avoid this trouble, we can use a smaller tube and ensure the perfect verticality of the tube. The flow in the form of a thin film also favors heat exchange, obtaining larger coefficients [12], in case that heating/cooling is necessary in the system. They are also useful when light penetration is not good in a batch reactor. Unfortunately, they are usually less applied for photochemical reactions.

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On the other hand, solar photo-Fenton in a compound parabolic collector (CPC) reactor is known to be one of the most environmentally benign and cost-effective systems for wastewater treatment [13–15].

In this work, a simple experimental falling film pilot plant has been constructed, tested and compared with a conventional artificial UV cylindrical reactor. Thus, results in the thin film device have also been compared with those obtained in a solar CPC plant. Carbamazepine (CBZ), a refractory pharmaceutical organic drug not degraded in WWTP processes (removal efficiencies below 10%) has been treated as a model pollutant and a previously optimized photo-Fenton process assisted with ultrasound radiation (US/UV/H_2O_2/Fe) has been used as an intensified AOP. The sonophotolytic degradation of organic compounds has already proved to be effective due to the synergistic effect of the US and UV irradiation [16].

In order to determine the efficacy of the thin film reactor approach as a process intensification technology for photocatalytic wastewater treatment, an economical analysis has also been made. There are many studies using thin film reactors with TiO_2 as a heterogeneous wastewater treatment [17–19]. However, to our knowledge no studies have been made in homogeneous phase comparing technical and economical efficiencies.

2. Experimental set-up

2.1. Laboratory scale device

The experimental set-up consists on two glass pipes bundled as a shell-and-tube heat exchanger (inner diameter = 2.75 cm; length = 28.3 cm). The CBZ solution flows in the form of a thin film that runs down inside the inner tube where a Heraeus UV immersed lamp TNN 15/32 is located. A pump is used to regulate the flow rate. A wider element in the upper part of the column acts as an overflow system which is responsible for the fluid falling as a film. The optical path lengths in this thin film reactor was obtained to be 1.23 cm. Due to the small dimensions of the thin film, it is ensured that all the radiation coming from the lamp is reaching the wastewater, enhancing the efficiency of the reactor.

2.2. Pilot plants

2.2.1. UV-pilot plant

The UV pilot plant (FLUORACADUS-08/2.2) is shown in Fig. 1 and is composed by a 28 L reactor (2240 mm × 730 mm × 100 mm), with four UV-C lamps (280–200 nm) TUV_TL_D_55W_HO_SLV UV-C PHILIPS. The system is able to treat up to 1400 L/h. Temperature (up to 60 °C) is controlled by a digital Fuji PXR4TAY1-1Vcontroller.

2.2.2. CPC pilot plant

The CPC consisted of a tank (50 L), a centrifugal recirculation pump, a solar collector unit with an area of 2 m^2 (concentration factor = 1) in an aluminum frame mounted on a fixed south-facing platform tilted 39° in Ciudad Real (Spain) with connecting tubing and valves. The solar unit had 16 borosilicate glass tubes (OD 32 mm) and the total illuminated volume inside the absorber tubes was 16 L. Visible solar radiation (400–600 nm) and UV radiation (200–400 nm) were measured by two Ecosystem model ACADUS radiometers which provided data for the incident UV-A solar power (W m^{-2}) and accumulated solar power (W h).

2.2.3. Thin film pilot plant

This pilot plant has the same configuration that the lab prototype, although now it consists on a two concentric stainless steel tube with higher dimensions (3.8 cm inner diameter; 85 cm height). A 55w submersible lamp (BIO-UV Ultraviolet solutions) was used.

2.3. Experimental runs and analysis

All experiments were carried out at pH = 2.7 and 30 °C. A 24 kHz, 200 W direct inmersion horn sonicator (UP200S with an S14 sonotrode, Hielscher) was used to generate ultrasonic sound waves in the sonoreactor in lab devices. The amplitude of the oscillatory system (power output) can be steplessly adjusted between 20% and 100%. The pulse mode factor (cycles) can be continuously varied between 10% and 100%. The set value equals the acoustic irradiation time in seconds, the difference to 1 s is the pause time. Thus, a setting of 1 implies that it is continuously switched on, whereas a setting of 0.6 means a power discharge of 0.6 s and a pause of 0.4 s. Amplitude and pulse length (cycles) were maintained constant at 60% and 1, respectively according to literature [11].

On the other hand, a UIP 1000HD230 (Hielscher) with a sound protection box was used in pilot plants installations (see Fig. S1 in Supplementary material). The main characteristics are: ultrasonic frequency of 20 kHz, automatic frequency tuning system, amplitude 25 μm adjustable from 50 to 100%, and dry running protected. The dimensions of the transducer are (L × W × H) 435 × 110 × 71 mm. The generator uses 230 V, AC, single phase, 8A, 50–60 Hz. A sonotrode (BS2d34) titanium, tip diameter 34 mm, length 125 mm was used.

More details of reactor configurations and ultrasound power are shown in Table 1. Initial concentration of carbamazepine (CBZ) in deionized water was 78.2 ppm (TOC = 55 ppm). The flow rate was 45 L/h in the thin film lab device, 1140 L/h in the conventional and solar pilot plants and 150 L/h in the thin film plant.

CBZ (99%) was obtained from Acros. Analytical grade ferrous sulfate ($FeSO_4{\cdot}7H_2O$), and 30% w/v hydrogen peroxide (H_2O_2) were acquired from Merck. The pH of the wastewater was adjusted with H_2SO_4 and NaOH solutions. Total organic carbon concentration was determined using a TOC analyzer (Shimadzu TOC-5000A).

Quantification of hydroxyl radicals was carried out using disodium salt of terephthalic acid (NaTA) [20]. NaTA (non-fluorescent) is known as an HO· scavenger; it reacts with HO· to form 2-hydroxyterephthalic acid (HTA, fluorescent). The concentration of HTA was determined by its fluorescence, which yield is proportional to the HO· concentration in the solution in the excess of NaTA.

The HTA fluorescence yield was measured with an RF 6000 spectro-fluorophotometer (Shimadzu). The excitation wavelength was set at 315 nm and the fluorescence spectra of the solution were collected in the range of 320–500 nm. The peak intensity was quantified for each solution at the emission wavelength of 425 nm using a previous calibration.

3. Results and discussion

3.1. Study of UV, US and UV/US processes

Fig. 2 shows degradation of CBZ under different processes (UV, US and UV/US) for the lab falling film device. The values of the photolytic constant (k_{UV}) were 0.0264 min^{-1} for CBZ degradation and 0.0019 min^{-1} for mineralization. The values of the sonolytic constant (k_{US}) were 0.0044 min^{-1} for CBZ degradation and 0.002 min^{-1} for mineralization. It was proved that hydrogen peroxide was either not formed under these conditions or it was below detection limits.

The synergism between the UV process and the sonolytic one can be quantified using the pseudo first order degradation rate constants according to Eq. (1) [9]: