



Coupling between high-frequency ultrasound and solar photo-Fenton at pilot scale for the treatment of organic contaminants: An initial approach



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ABSTRACT

This study aims to evaluate the performance of a novel pilot-scale coupled system consisting of a high frequency ultrasonic reactor (400 kHz) and a compound parabolic collector (CPC). The benefits of the concurrent application of ultrasound and the photo-Fenton process were studied in regard to the degradation behavior of a series of organic pollutants. Three compounds (phenol, bisphenol A and diuron) with different physicochemical properties have been chosen in order to identify possible synergistic effects and to obtain a better estimate of the general feasibility of such a system at field scale (10 L). Bisphenol A and diuron were specifically chosen due to their high hydrophobicity, and thus their assumed higher affinity towards the cavitation bubble. Experiments were conducted under ultrasonic, photo-Fenton and combined treatments. Enhanced degradation kinetics were observed during the coupled treatment and synergy factors clearly in excess of 1 have been calculated for phenol as well as for saturated solutions of bisphenol A and diuron. Although the relatively high cost of ultrasound compared to photo-Fenton still presents a significant challenge towards mainstream industrial application, the observed behavior suggests that its prudent use has the potential to significantly benefit the photo-Fenton process, via the decrease of both treatment time and H₂O₂ consumption.

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1. Introduction

Advanced oxidation processes (AOPs) are a set of technologies which lead to the oxidation of pollutants by provoking the formation of highly reactive oxygen species, especially ·OH radicals. Among the most well known AOPs is the photo-Fenton process, a non-selective photocatalytic process in which ·OH is generated during the oxidation of Fe²⁺ to Fe³⁺ by H₂O₂. Application of ultraviolet light at frequencies below 400 nm (present within the spectrum of solar radiation) can regenerate the Fe²⁺, greatly increasing the efficiency of the process [1–3]. It has been studied extensively for the treatment of many types of contaminants [4,5] at relatively low cost [6]. As such, the photo-Fenton process can provide the industry with a powerful tool to treat wastewater with clean energy from the sun [7]. However, the process is not a universal remedy as it can demand large amounts of H₂O₂ and

its dependence on light, can be a limiting factor in sunshine deprived regions. Iron also tends to form insoluble aqua complexes at pH above 4, sometimes necessitating either pH adjustment or the addition of iron-chelating agents for increasing its solubility in neutral pH [8]. In order to minimize treatment time, reagent consumption and costs, significant investigative efforts have been made towards the development of hybrid processes such as biological treatment/photo-Fenton [9,10], electro-and photoelectro-Fenton [11], and ultrasound/photo-Fenton [12]. It is this latter system that will be the focus of this study.

Ultrasonic (US) treatment is another AOP that has been gaining interest in the last years. When ultrasound is applied to a liquid medium, cavitation bubbles are formed. After a series of expansion and compression cycles, these bubbles violently collapse to generate very high temperatures and pressures concentrated in one localized ‘hot spot’ [13]. The surrounding liquid will consequently quench it within a millisecond timeframe (cooling rates in excess of 10¹² K/s [14]), generating extreme gradients of both pressure and temperature. This quasi-adiabatic energy process has profound

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effects on the surrounding liquid [15] as well as the chemical species found in its vicinity. It has been reported that reactive radicals such as $\cdot\text{OH}$ [16] can be generated via the thermal dissociation of water [15] during bubble collapse. As the $\cdot\text{OH}$ radical has a short lifetime [17], hydrophobic compounds are expected to be preferentially oxidized near the bubble/bulk interface due to their close proximity to the cavitation bubble [18–20]. Additionally, if their vapor pressure is high, they may enter the bubble and be directly pyrolyzed during its implosion. It has also been shown at laboratory scale that ultrasound can promote the generation of H_2O_2 which could be utilized during the photo-Fenton reaction [21]. It is however unverified whether this generation remains significant at pilot-scale. H_2O_2 maintains a complex role in pure ultrasonic processes as well, acting both as a source of free radicals by a dissociation process, as well as a radical scavenger [22].

High ultrasound frequencies are widely regarded as more efficient in the destruction of organic pollutants, with several studies pointing towards an optimal frequency region between 350 and 500 kHz, with representative reported values at 358 kHz [23], 506 kHz [24] and 582 kHz [25]. Due to the high cost implicit to the use of pure ultrasound treatment, there is a strong interest in combining it with other AOPs and taking advantage of beneficial synergistic effects for lowering treatment costs.

Such combinations have therefore been the focus of several interesting investigative efforts. Hybrid treatments with photo-Fenton [21], TiO_2 heterogeneous photocatalysis [19,26], ozone [27] and ozone/UV [28] have been attempted with significant success. To the best of our knowledge, the presented hybrid system has never been tested under solar illumination and at pilot scale.

This research focuses on the application of high frequency ultrasound as a complement to the solar photo-Fenton process in a 10 L pilot plant reactor system. A combined process could: (I) take advantage of excess hydrogen peroxide produced from hydroxyl radical recombination during the ultrasonic treatment for promoting Fenton type reactions, (II) enhance degradation kinetics by the preferential treatment of different types of compounds by each process (hydrophobic and hydrophilic contaminants by ultrasounds and photo-Fenton, respectively), (III) allow better homogenization of hydrophobic contaminants suspended in water by promoting the formation of smaller droplets, thus forming emulsions and/or stabler suspensions [29] and (IV) minimize the use of reagents (Fe and H_2O_2) and thus limit secondary pollution and costs.

Three different contaminants were chosen to evaluate the efficiency of the combined treatment, phenol, bisphenol A (BPA) and diuron. Phenol is a fairly water soluble compound having a

multitude of industrial uses in the plastics, herbicide and pharmaceutical industries. It has been used extensively in the study of AOPs as a model compound, even used for the development of standardization protocols [30]. Bisphenol A is a hydrophobic monomer widely used as a precursor for the production of resins and polymers. Diuron is the commercial name of DCMU (3-(3,4-dichlorophenyl)-1,1-dimethylurea), a highly hydrophobic photosynthesis inhibitor herbicide. Their structures as well as some of their physicochemical properties are given in Table 1.

2. Materials and methods

2.1. Reagents

Phenol (99% purity) and bisphenol A (99% purity) were acquired from Sigma Aldrich. Diuron (97% purity) was supplied from Aragonesas Agro, S.A. (Spain). Solutions were prepared with distilled water from the Plataforma Solar de Almeria distillation plant. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ and H_2O_2 (33% w/v) were obtained from Panreac (Spain). Acetonitrile (ACN), formic acid (FA) and water used for liquid chromatography analyses were all HPLC-grade.

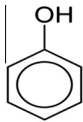
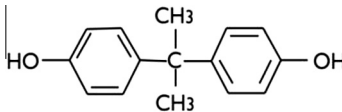
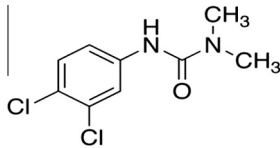
2.2. Analytical methods

Pollutant concentration measurements were made with an Agilent 1100 series High Pressure Liquid Chromatography (HPLC) equipped with a C18 column (Supelcosil LC-18, 5 μm particle size, length 15 cm, i.d. 3 mm). The Agilent Chemstation LC3D software was used for the analysis. All samples were diluted by a factor of 2 in acetonitrile and filtered through a 0.2 μm syringe-driven filter prior to analysis. The injected volume for all samples was 20 μL . The analytical conditions for each pollutant can be seen in Table 1.

Total organic carbon was measured by a Shimadzu TOC- V_{CSN} analyzer equipped with an ASI-V automatic sampler.

Hydrogen peroxide concentrations were measured spectrophotometrically, using titanium (IV) oxysulfate following DIN 38402H15 (5 ml of sample solution were added to 0.5 ml of titanium (IV) oxysulfate and the absorbance measured at 410 nm). Total iron concentrations were estimated by complexation with 1,10 phenanthroline and absorbance measurements at 510 nm, a method following ISO 6332. All spectrophotometric measurements were made with a UNICAM UV/VIS spectrophotometer controlled with VISION software. Chloride anions (for following diuron degradation) were determined with a Dionex DX-600 ion chromatograph system equipped with an autosampler (Dionex AS40), a

Table 1
Structure, physicochemical properties and HPLC parameters of phenol, bisphenol A and diuron.

	Phenol ^a	BPA ^b	Diuron ^c
Chemical structure			
Solubility in H_2O (mg L^{-1})	8.2×10^4	ca. 300	42
logKow	1.46	3.4	2.77
P_v (mmHg)	0.46	7.24×10^{-7}	3.1×10^{-6}
Wavelength (nm)	272	280	
Eluent composition (v/v)	58:42 (0.5% FA/ACN)	50:50 (0.5% FA/ACN)	
Eluent flow (mL min^{-1})	0.5	0.5	
Retention time (min)	7	5	

Physicochemical properties acquired from:

^a Sangster, Journal of Physical and Chemical Reference Data.

^b Bayer Product Safety Data Sheet on BPA.

^c Pesticide information profiles, EXTTOXNET (Extension toxicology network).

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