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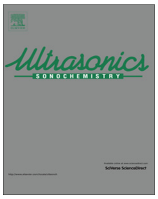

Ultrasound enhancement of near-neutral photo-Fenton for effective *E. coli* inactivation in wastewater

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ABSTRACT

In this study, we attempt for the first time to couple sonication and photo-Fenton for bacterial inactivation of secondary treated effluent. Synthetic wastewater was subjected to sequential high-frequency/low power sonication, followed by mild photo-Fenton treatment, under a solar simulator. It was followed by the assessment of the contribution of each component of the process (Fenton, US, hv) towards the removal rate and the long-term survival; sunlight greatly improved the treatment efficiency, with the coupled process being the only one to yield total inactivation within the 4-h period of treatment. The short-term beneficial disinfecting action of US and its detrimental effect on bacterial survival in long term, as well as the impact of light addition were also revealed. Finally, an investigation on the operational parameters of the process was performed, to investigate possible improvement and/or limitations of the coupled treatment; 3 levels of each parameter involved (hydraulic, environmental, US and Fenton) were tested. Only H_2O_2 increased improved the process significantly, but the action mode of the joint process indicated potential cost-effective solutions towards the implementation of this method.

1. Introduction

Advanced Oxidation Processes (AOPs) have been in the spotlight for more than three decades, as part of a global effort to modernize actual methods of water disinfection. Their action is based on the production of the extremely oxidizing hydroxyl radical ($^{\cdot}OH$) [1], which can attack the chemical structure of the microorganisms' cell wall and inactivate them [2]. Ultrasound has been extensively studied as an AOP, targeting microorganism inactivation, such as bacteria, viruses etc., by either low (~20 kHz) or high frequencies (200+ kHz) [2–4] and [5]. This method is exploiting the direct mechanical action of the cavitation bubble implosion (low frequencies) as well as the additional production of H_2O_2 and $^{\cdot}OH$ radicals during cavitation (high frequencies); the propagation of ultrasound waves in the aqueous medium initiates the aforementioned actions, by the generation of extreme temperature and pressure conditions [6], which have a proven bactericidal effect [7–9], and [10].

As far as the ultrasound set-up is concerned, the frequency of the ultrasonic waves is a crucial parameter, for it defines the size of the cavitation bubbles [11]. Literature suggests that the average cavity size is proportional to the acoustic power and inversely proportional to the ultrasound frequency [12]. It is also verified that apart from low frequency/high power ultrasound systems [13,14], high frequency/low power processes have been proven to efficiently inactivate microorganisms [8,15,16]. However, ultrasound already requires high intensities to achieve total inactivation of microorganisms, and therefore, is considered an expensive application for large volumes of water [2]. Considering all the above, it should be used preferably as a complementary disinfecting method [2].

The photo-Fenton process [17] could play the role of the main disinfecting method, as one of the most efficient methods of hydroxyl radical production [18]. Lately, it has even been used to disinfect drinking water, being a good alternative to chlorination, with its known disinfection by-products formation [19]. However,

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wastewater is a complex matrix in which many organic and inorganic compounds coexist, such as nutrients, salts and many substances that could influence the outcome of the application of either process. It has been reported that the presence of hydroxyl radical scavengers, namely the organic matter, presents an additional oxidation target and renders AOPs sensitive to the treatment of wastewater [20,21]. Suppression of these scavengers revealed their importance [10] and also, for years the Fenton reaction was believed to be a pH-restricted reaction in highly acidic regions; it was considered impossible to apply such methods, in matrices with near-neutral pH [22]. However, recent advances [18,23] and [24] have proven its effectiveness in the neutral area, and in the simultaneous presence of organic matter [18,25]. Previous work in our group has shown, there is no need for acidification prior to the treatment to keep a significant part of the iron soluble; apart from the direct complexion with bacteria, there are some strong photoactive Fe^{3+} complexes formed in presence of organic matter [21,25]:

$$[R - COO^- - Fe^{3+}]^{2+} \rightarrow hv \rightarrow Fe^{2+} + CO_2 + R^{\cdot} \quad (1)$$

The cycle continues with the reaction of the regenerated iron with hydrogen peroxide to produce more hydroxyl radicals etc.

$$Fe^{2+} + H_2O_2 \rightarrow OH^- + {}^{\cdot}OH + Fe^{3+} \quad (2)$$

In order to increase the amount of water treated by solar-assisted methods, compound parabolic collector reactors have been used [17,18,23] and [26], and solar photo-Fenton even was a subject under question, because of the intermittent action of the light [27]. There is a technical issue to be addressed in the intermittent nature of this treatment method, and the existence of “dead” time among the experiment. Typically, a CPC photo-reactor consists of the illuminated surface and the storage-recirculation tank. The recirculating flow of these reactors creates a gap in the illumination for as long as water is present in the (dark) storage tank, allowing bacterial defense mechanisms to deploy [28]. Literature indicates a variety of light-to-dark distributions (Table 1), which materialize this difference [17,18,23,26,29–31].

Therefore, keeping in mind the improvement of the near-neutral photo-Fenton disinfection while working within realistic operational parameters, for the first time we study the joint ultrasound/photo-Fenton treatment for wastewater, in a CPC-like, lab-scale system. In this manner, we will take advantage of two factors that could work complementing each other: firstly, the exploitation of the dark intervals for sonication, along with the utilization of solar energy for the promotion of a mild photo-Fenton reaction and secondly, the supplementary action these processes have, since, for instance, US can produce H_2O_2 and subsequently, could fuel the photo-Fenton process. In our study, synthetic secondary effluent was used, spiked with *Escherichia coli* K12, recirculating around a sonicated dark reactor and an illuminated batch reactor, under solar simulated light. We aim to:

(i). Explore the effects of the photo-Fenton factors (light, reactants) and the ultrasonic action (US) on both short and long-term disinfection events; clarification of the effects is attempted by stepwise insertion of the participating actions.
(ii). Investigate the involved operational parameters (recirculation speed, temperature, light intensity, treated volume and distribution of volumes, iron and hydrogen peroxide content, ultrasound intensity) in a small-scale set-up.

2. Materials and methods

2.1. Synthetic secondary effluent preparation

2.1.1. Microbial methods

The *E. coli* strain K12 (MG1655) employed was provided by the “Deutsche Sammlung von Mikroorganismen und Zellkulturen”. Luria–Bertani broth was inoculated with a colony from bacterial *E. coli* pre-cultures, placed in 50 ml plastic falcons for 8 h and then loop inoculated, after 1% dilution overnight (180 rpm and 37 °C for 15 h), to achieve stationary phase cells.

Harvested cells were centrifuged and washed three times (5000 rpm, 15 and 5 min for separation and washing, respectively), followed by reservation in saline solution (neutral pH solution with 8 g/L NaCl and 0.8 g/L KCl); a solution of 10^9 CFU/mL is achieved.

2.1.2. Synthetic wastewater composition

The preparation of the synthetic wastewater took place as under the directive of SYMAWE [32]. The initial DOC was 100 mg/L (250 mg/L COD). The experiments used a 10% dilution (in distilled water) of the said composition. The dilution performed corresponds to the COD and DOC values encountered in normal secondary effluents. Finally, the pH of the sample was between 6.5 and 7. 1 mL of the prepared bacterial solution was used to spike the diluted wastewater, thus resulting in an initial bacterial population of 10^6 CFU/mL.

2.2. Reagents and analyses

The wastewater constituents, as well as the Fenton reagents were used as received. Photo-Fenton experiments were carried out employing ferrous sulfate heptahydrate (Fluka Chemika), hydrogen peroxide (35% by weight, Sigma Aldrich), used as received. The dissolved iron (Fe^{2+}, Fe^{3+}) was measured with the ferrozine method [33], using a UV–Vis Lambda 20 spectrophotometer, provided by PerkinElmer, Schwerzenbach, Switzerland. For 1.6 mL of sample 0.2 of ferrozine solution (4.9 mM) was added, followed by 0.2 mL of hydroxylamine hydrochloride solution 10% w/w.

Table 1
Hydraulic characteristics of previous works in CPC reactors.

	Flow rate (L/min)	Total volume (L)	Volume-to-flowrate ratio	Illuminated volume (%)	Volume in the dark (%)	Light-to-dark ratio
Fernandez-Ibañez et al. (2009)	20	14	0.70	32	68	0.47
Moncayo-Lasso et al. (2009)	17.5	20	1.14	45	55	0.82
Fernandez-Ibañez et al. (2005) (varied flowrates)	5, 13, 22.5	11	2.2, 0.85, 0.49	49	51	0.96
Rincon & Pulgarin (2007) (min, max capacity)	20.5	37, 70	1.80, 3.41	65, 34	35, 66	1.86, 0.52
Sciacca et al. (2011)	24.2	18	0.74	83	17	4.88
Giannakis et al. (2013)	0.03, 0.06, 0.07	0.7	22.58, 12.28, 9.59	33	67	0.49
Ndounla et al. (2013)	2	25	12.5	60	40	1.53