Abstract

The effects of operational parameters upon the hydroxyl radical generation of sonochemical reactors are critical to optimize this technology for wastewater treatment purposes. Ultrasonic wave characteristics are usually considered as the main parameter to be taken into account. Nevertheless, it is the interaction of these waves with the liquid medium and the reactor what really affects the process. Therefore, the characterization of sonochemical reactors should be based on the effective pressure distribution in the reactor, which not only includes the wave characteristics but also the propagation and reflection of these ultrasonic oscillations. The pressure field can be characterized using different parameters, such as maximum pressure amplitude or volumetric integration of pressure in the reactor. This study intends to find a correlation between such calculated pressure-distribution-related parameters and experimental measurements of hydroxyl radicals in the process. Both experiments and calculations are run varying the tip-bottom distance (keeping the rest of parameters constant), creating different reflection effects with the reactor walls and therefore different pressure distributions across the reactor. The hydroxyl radical measurements are performed with salicylic acid dosimetry, applying a specific developed method for biphasic cavitating systems. On the other hand, the pressure distribution was calculated simulating the different configurations with the computational tool COMSOL.

Keywords: Characterization; computational tool; dosimetry; hydroxyl; radical; reflection; salicylic acid; ultrasonics and wave

1. Introduction

Under certain conditions, when a liquid is irradiated by a high power ultrasonic wave, radially oscillating micron-sized bubbles appear and subsequently collapse following the changes in the external pressure. This phenomenon is known as acoustic cavitation [1,2]. The sudden collapse following the expansion of the bubbles generates a compression effect over the internal gases, inducing extreme pressure and temperature conditions inside and near the...
bubbles. This process gives rise to chemical mechanisms, and is usually known as sonochemistry [3]. The sonochemistry can be considered as an AOP (Advanced Oxidation Process), and its application for water treatment has long been considered as a promising technology [4,5]. The study of acoustic cavitation has been approached from different perspectives: purely experimental chemical approaches (direct evaluation of experimental results) [6]-[9], purely theoretical approaches (simulation of single bubbles or even bubble clouds) [10,11] and parametrical studies taking into account both experimental results and theoretical predictions. This study tries to apply the latter combined approach by correlating parameters obtained from simulations of the physical behaviour of the reactor with experimental results obtained from hydroxyl radical traps. By doing so, the authors intend to evaluate the (more convenient) simulation tools in predicting reactor design effects over the efficiency of the process.

1.1. Sonochemistry: Chemical effects of acoustic cavitation

The chemical degradation of organic pollutants is directly related to the amount of (extremely oxidant) hydroxyl radicals generated. Therefore, monitoring the generation of ·OH radicals in sonochemical reactions is essential to understand the potential applicability of ultrasonic cavitation as an AOP. Several indirect techniques of radical quantification have been developed during the last decades such as the ESR spin-trapping using nitroxide 5,5-dimethyl-1-pyrroline-N-oxide (DMPO), the Fricke dosimetry [12,13], iodide dosimetry [14] and terephthalate [15-17] or salicylic acid dosimetry [18]. These methods are based on the quantification of the reaction products of the process, which are indirectly related to the ·OH radicals that have participated in the specific reaction (the so-called dosimeters). The main differences between the dosimeters are the type of scavenger (reactant) used in each case, the specificity of each process and the determination of the reaction products.

The hydroxyl radicals are generated inside the bubbles (i.e. in the gas phase). Therefore, in order to react with the substances in the liquid phase (e.g. the dosimeter) they have to diffuse through the gas phase, the interface and the liquid phase. In this process, the radicals tend to recombine, eventually leading to an underestimation of the OH generation [18].Thus, dosimetry in cavitation systems has to guarantee the accessibility of the scavenger to the ·OH radicals. Taking into account our previous studies in hydrodynamic cavitation, we have selected salicylic acid dosimetry as the method to estimate the ·OH radical generation in the cavitation process. This dosimeter offers a number of advantages:

1. Specificity, meaning that the hydroxylated products measured are exclusively due to the action of ·OH radicals. No intermediate products affect the results.
2. The reaction products of salicylic acid dosimetry can be easily separated with HPLC and detected using either diode array (or UV) detector or induced fluorescence detector [18].
3. The weak acidity of salicylic acid can be used to control the relative concentration of neutral/ionic salicylic acid by adjusting the pH [18,19].
4. Salicylic acid is a non-polar and slightly soluble substance. This means that it is possible to reach a relatively high concentration of dosimeter (easily dissolved by increasing the pH), with a subsequent protonization of the ionic form (by decreasing the pH) to guarantee that the majority of the non-polar salicylic acid accumulates in the gas-liquid interface of the bubbles, thus being more available for the diffusing ·OH radicals formed in the gas phase.
5. The kinetics of salicylic acid hydroxylation is favoured versus other dosimeters.

1.2. Physical propagation of waves

The sono-reactor is composed by the liquid solution, in which the ultrasonic waves are transported, and the solid parts (the walls, bottom and emitter). The linear propagation of an acoustic wave is described by the linearization of the Euler equations, assuming mono-harmonic waves at angular frequency. The continuity equation is used as a boundary condition for the equation governing the vibration of the solid. The propagating waves are reflected by the reactor walls, giving rise to constructive and destructive interferences. These constructive/destructive effects depend
on the distance between ultrasonic tip and reactor bottom and the reactor design, and are essential to obtain an energy efficient sonochemical process.

2. Materials and methods

The sonochemical reactor consists on a glass container filled with salicylic acid dissolved (100 ppm) in deionized water (500 ml). The ultrasonic waves were emitted by a sonicator or sonotrode (Model VC-750, Sonics and Materials, 750W) at 80% amplitude. The titanium horn tip (Model CV33) was 13 mm in diameter. Frequency of the sound wave was kept constant at 20 kHz. Solution temperature (20ºC) was controlled by immersing the reactor into a water bath with a cooling unit (Frigedor-Reg, Selecta). The pH was adjusted with HCl 6 M before starting each experiment. The pH after the experiment was also controlled with no significant variations observed. The distance between the sonotrode tip and the reactor bottom was modified in each essay using the same values as in the computational simulations.

The reactants, provided by Aldrich, were: 2,5-dihydroxybenzoic acid (2,5-DHB) 99%, 2,3-dihydroxybenzoic acid (2,3-DHB) 99% and salicylic acid 99%. The determination of the reaction products of salicylic acid was made with a High Performance Liquid Chromatographer (Shimazdu) equipped with a Diode Array detector. The column was a X-Terra C18 of 10 cm length and 3.0 cm i.d. The mobile phase consisted of 55% phosphate phosphoric (pH 2.5)/45% methanol in isocratic mode at a flow-rate of 1.0 mL/min.

![Laboratory equipments’ configuration](image1)

Fig. 1  Laboratory equipments’ configuration

![Hydroxylation of salicylic acid](image2)

Fig. 2  Hydroxylation of salicylic acid
Hydroxyl radicals readily hydroxylate the aromatic ring of salicylic acid (figure 2). Therefore, each mole of ·OH radicals generated in the process is supposed to generate a mole of reaction product (2,5-DHB or 2,3-DHB). Thus, by measuring the reaction products we can evaluate the efficiency of the process in terms of degradation capability. The number of hydroxylated products is used as the main variable to be correlated with the response variables of the simulations.

The experimental configuration was simulated with the Acoustic-Structural Modules of COMSOL software. As shown in figure 3, the axial geometry of the reactor allowed for a representation of half of the transversal plane. The sonotrode emits from above in a liquid in contact with air on its upper surface, and limited laterally by thin glass walls. The sonotrode is assumed to vibrate vertically with an amplitude of $124 \cdot 10^{-6} \text{m}$.

Liquid properties are taken as $\rho_{\text{liq}} = 1000 \text{ kg m}^{-3}$ and $c_{\text{liq}} = 1500 \text{ m s}^{-1}$. The elastic properties are $E = 73 \text{ GPa}$, $\nu = 0.17$ for glass. The liquid height is fixed to $h = 87 \text{ mm}$, counted from the bottom of the reactor. The parameter of study is the distance between the vibrating sonotrode and the bottom of reactor. That distance is varied, both in experimental essays and in simulations, using the following values: $\lambda/8, \lambda/4, \lambda/3, 3\lambda/8, \lambda/2, 5\lambda/8, 2\lambda/3, 3\lambda/4, 7\lambda/8, \lambda$, being the wave length in water $75 \text{ mm}$.

The response variables of the simulations (to be correlated with the experimental results) are: the pressure amplitude (maximum minus minimum absolute pressure in each ultrasonic cycle) and the volume integral of pressure amplitude in the reactor.

3. Results and discussion

A batch of ten essays was repeated 3 times in order to estimate the formation of ·OH radicals at different values of tip to bottom distance. As shown in figure 8, the repetitions yielded similar tendencies. Nevertheless, the efficiency decreased in subsequent experiments. This decrease has previously been observed and is considered to be related to the degradation of the titanium tip. All results were normalized to eliminate this effect.

On the other hand, as shown in figures 6 and 7, the computational simulations revealed a significant effect of the walls and their properties on the final results. As shown in figures 4 and 5, under the selected conditions, regardless of the considered response variable, the maximum efficiency of the reactor takes place when the tip to bottom
distance is around \( \lambda/3 \) or \( \lambda \), whilst the minimum efficiency is observed around \( 5\lambda/8 \). No significant difference is observed between the two maxima.

Experimental results do not take into account the recombination of \( \cdot \text{OH} \) radicals, the degradation of the reaction products or the generation of other by-products. Neither does it consider the existence of other oxidation mechanisms which are not related to hydroxyl radicals. On the other hand, the linear equation system solved by the simulation does not take into account the attenuation factors (e.g. from bubble cloud). Moreover, it is difficult to consider additional factors such as non-homogeneous liquid properties and/or the existence of weak points in the liquid (e.g. bubbles, solid particles, etc).

Despite the aforementioned inaccuracies of both experimental and theoretical methods, the authors expected to observe a certain degree of correlation between the theoretical and the experimental results. In general, larger pressure amplitudes and/or a higher energy efficiencies (represented by the volumetric integral of pressure amplitude) should generate more energetic bubble clouds, and therefore a larger amount of \( \cdot \text{OH} \) radicals. Thus, the constructive/destructive interferences should lead to a sinusoidal form (in both experimental and theoretical data) with a wavelength in the order of \( \lambda \). Both the experimental and theoretical results followed approximately this expected wave shape. The experimental data also shows a consistent reproducible form, although this is only attained after the normalization of each essay referring the concentration of hydroxylated products to the maximum value obtained in each essay.

Nevertheless, the direct comparison shown in figure 9 indicates a clear displacement of the experimental data to the right. This displacement is easily explained by the numerous assumptions made both in the experimental and theoretical methodology. The computational tool would demonstrate to be a valid alternative if this displacement was constant and/or at least predictable. Future studies will concentrate on adjusting the simulation parameters and introducing attenuation factors related to the biphasic medium formed by the cavitating cloud to correct the observed error.

Fig.4 Maximum/minimum pressures reached in the reactor during a single ultrasonic cycle versus tip-bottom distance (simulations)
Fig. 5  Volumetric integral of pressure in the reactor versus tip-bottom distance (simulations).

Fig. 6  Simulation for distance=46,875 mm, which constitutes the less efficient case of study.
Fig. 7 Simulation for distance=75 mm, which constitutes the most efficient case of study.

Fig. 8 Normalized hydroxylation of salicylic acid versus tip-bottom distance (3 experiments).
4. Conclusions

The observed deviation between experimental data of ·OH production and the parameters obtained from pressure field simulations in a sonochemical reactors demonstrates that further adjustments have to be made in order to use this computational tools for the optimization of sonochemical reactors design. Nevertheless, the results suggest that the theoretical observations are merely displaced, and that simple adjustments in the simulation parameters could lead to a fairly accurate theoretical tool. However, some of these adjustments might involve more complex biphasic models, particularly those related to the bubble cloud attenuation of the pressure waves.

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