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Salicylic acid dosimetry applied for the statistical determination of significant parameters in a sonochemical reactor

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ABSTRACT

The effects of operational parameters upon the hydroxyl radical generation of sonochemical reactors are critical to optimize this technology for wastewater treatment purposes.

Salicylic acid dosimetry, due to its chemical and physical properties, is a very adequate method to characterize a sonochemical reactor by indirect determination of the $^{\bullet}$OH radicals generated in the cavitating process. The degradation products, 2,5-dihydroxybenzoic acid (2,5-DHB) and 2,3-dihydroxybenzoic acid (2,3-DHB), are specific and easily determined with HPLC methods. The most significant parameters were determined by designing a 2^5 factorial set of experiments and applying some statistical tools to the results obtained with the dosimeter. When operating within a limited range (typical range of standard sonochemical reactors) the statistical tools showed that only the dosimeter concentration and the reactor geometry were mathematically significant in the process.

1. Introduction

The use of sonochemistry as an advanced oxidation process (AOP) for water treatment has long been considered as a promising technology [1–3]. It is usually accepted that the parametrical dependence of $^{\bullet}$OH radicals generation and oxidation potential of sonochemical reactors is one of the keys to develop this technology. There are a number of parameters that have been studied, among them, the most important are the following [4]: solution temperature [5], ultrasonic intensity [6–8] and its frequency [6–9], initial concentration of substrate, the amount and/or nature of dissolved gases [6–10], or substances [5,10,11], existence of radical scavengers or surfactants, geometrical factors such as sample volume and resonance of ultrasonic waves in the reactor [7,12,13]. Most of the referenced works are devoted to study the effect of each individual parameter on the degradation of some specific organic pollutants. Although such works constitute a useful tool to demonstrate the applicability of sonochemical reactors to degrade these particular substances, there are two important aspects which have often been disrigarded: first, the degradation of each pollutant takes place in a different manner, and second, the direct observation of individual parameters might be intuitive and useful, but does not provide consistent information in respect to the relative importance and/or interdependence of this parameter with the rest of the operational variables. Consequently, some of the experimental studies in bibliography are difficult to compare or reproduce and not all the conclusions are consistent or coherent. It is therefore difficult to draw a common picture regarding parametric behaviour and optimization of sonochemical reactors.

Although sonochemistry has demonstrated to be a valid and clean source of $^{\bullet}$OH radicals, the industry demands further evidences of its effectiveness for real applications versus other alternative technologies. Theoretically, cavitation offers an important advantage over conventional AOPs: not using additional reactants (which should reduce both the operational costs and the secondary products [14]). Nevertheless, in order to be an applicable and competitive technology, researchers need to find the tools to reach a consistent common ground in the parametrical studies of reactors. Thus, to evaluate, compare and eventually optimize different experiments and reactors it is recommendable to use representative substances/reactions to standardize the characterization of the process, and mathematical tools to extract conclusions from the results.

1.1. Hydroxyl radical dosimeters and design of experiments

Specific hydroxyl radical dosimeters are adequate substances to standardize the characterization of sonochemical processes. Mon-

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itoring the generation of •OH radicals in sonochemical reactions is essential to know 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 nitrone 5,5-dimethyl-1-pyrroline-N-oxide (DMPO), the Fricke dosimetry [15,16], iodide dosimetry [17] and terephthalate [9,18–20] or salicylic acid dosimetries [21,22]. 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 main differences between the dosimeters are the type of scavenger used, the specificity of each process and the determination of the reaction products.

In cavitation processes, 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) the radicals 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 radicals generation [21]. Thus, dosimetry in cavitation systems has to guarantee the accessibility of the scavenger to the •OH radicals. Some authors have applied Fricke dosimetry to ultrasonic reactors [9,16,20] while only a few have used specific dosimeters such as terephthalate [9,18–20] or salicylic [23]. Taking into account our previous studies in hydrodynamic cavitation, we have selected salicylic acid dosimetry as the method to estimate the •OH radicals generation in the cavitation process. This dosimeter offers a number of advantages:

1. Organic dosimetries are specific, 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 [21].
3. The weak acidity of salicylic acid can be used to control the relative concentration of neutral/ionic salicylic acid by adjusting the pH [21,23].
4. Salicylic acid is a non-polar and slightly soluble substance. Therefore, 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, hence 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.

Terephthalic acid represents an interesting alternative among specific dosimeters. Nonetheless, although advantages 1–3 also apply, points 4 and 5 are not as favourable as in salicylic (i.e. terephthalic acid is much less soluble and the reaction with •OH is slower).

This work intends to test the applicability of salicylic acid dosimeter in a biphasic ultrasonic cavitation system by using this dosimeter for the characterization of a sonochemical reactor. A second objective of this study is to provide statistical evidence of the significance of the most commonly studied sonochemical parameters in the process by applying statistical methodologies and tools while minimizing the number of required experiments. The latter objective will be fullfiled through the application of design of experiments (DOE), or more concretely, implementing a methodology based on creating a central composite design to fit a statistical model to the experimental data and determine the statistical significance of combined factors on a selected response [24]. DOE provides the tools to minimize the number of required experiments to obtain valid conclusions while also helping to analyse both the individual factors and the interactions between them. This study is specially focused on reaching the first step of the DOE, the screening of important factors by performing a previous full factorial design.

A complete factorial design to optimize sonochemical reactors/processes would require a tremendous experimental effort. This study is limited to the experimental range in which the most common sonochemical reactors work. Therefore, the results are not valid for overall optimization purposes. Nonetheless, this study provides useful information to determine those parameters that have to be taken into account when comparing or reproducing results in different reactors/conditions, or in other words, this work intends to determine if two experiments under similar conditions should give rise to similar results, and if not, which parameters are most likely to be causing the observed differences.

2. Experimental

Experiments were conducted in a glass reactor containing salicylic acid dissolved (50 or 200 mg/l) in deionized water (200 or 400 ml). Ultrasonic waves were emitted by an ultrasonic source (Model VC-750, Sonics & Materials Inc., Newtown, CT, USA, 750 W) at 60 or 80% amplitude (40 or 70 $W/cm^2 \pm 4$). The titanium horn tip (Model CV33) was 13 mm in diameter. Frequency of the sound wave was kept constant at 20 kHz.

Solution temperature (10 or 20 °C ± 1) was controlled by immersing the reactor into a water bath with a cooling unit (Frigedor-Reg, JP Selecta) and measured by a temperature sensor connected to a digital indicator screen. As aforementioned, ultrasonic pulses generate energy that is transmitted to the sample. A previous study in heat exchange was conducted in order to optimize the appropriate water bath temperature for each case. The pH was adjusted to a range between 2 and 2.5 adding drops of HCl 6 M at the beginning of each experiment. The pH after the experiment was also monitored. No significant differences were observed. The distances were selected considering the wavelength of an ultrasonic wave of 20 kHz in water (75 mm) and the wave interference theory. Waves are destructive when their phase lag equals $n\lambda/2$ and constructive when it is equal to $n\lambda$ (n being an integer). We have chosen two intermediate values, $3\lambda/8$ and $\lambda/4$, to study the influence of this parameter on the degradation rates. The immersion depth of the probe could also be considered as an experimental parameter, nevertheless being dependent on the tip to bottom distance and the liquid volume, it will not be taken into account in the parametrical study. The depth of the probe was 41.9 and 51.2 mm for reactor 1 (400 ml) and 15.9 and 25.2 mm for reactor 2 (200 ml), in both cases at tip-bottom distances of $3\lambda/8$ and $\lambda/4$, respectively.

The reactants, provided by Sigma–Aldrich, included 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 performed 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.

3. Selected parameters

The salicylic acid dosimetry is applied, as previously explained, to study the influence of five selected parameters on the sonication process. Hence, parameter related to the wave, the sample the dosimeter and the geometry of the reactor were taken into account in order to determine the most important influences on the response. The following parameters were selected in the statistical factorial study.

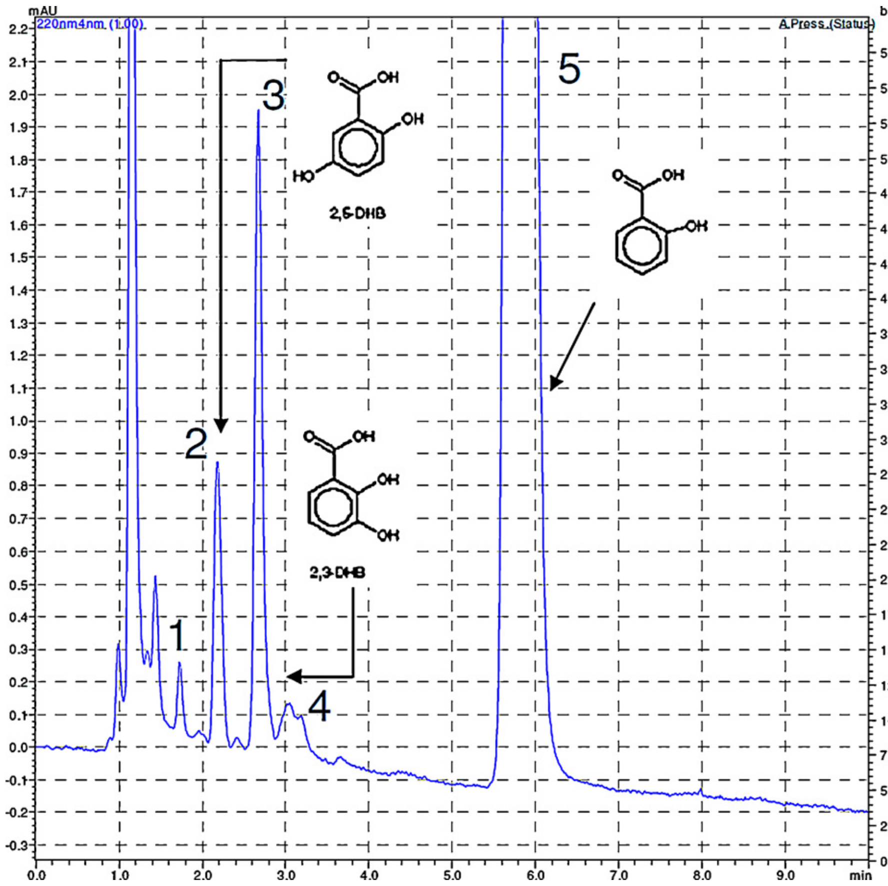

Fig. 1. Typical chromatogram of the hydroxylated derivatives and salicylic acid after 90 min of sonication.

- Wave factor (intensity): *sonochemical intensity* was selected as the representative parameter of ultrasonic waves. As the power supply increases, the sonochemical effects increase as well. This is due to the influence of intensity on the collapse temperature and pressure. Higher intensities give rise to more violent bubble collapse. However, excessive intensity might lead to an excessive bubble growth and to a decrease in the overall effectiveness of the process [4].
- Sample factors (temperature): the influence mechanism of *temperature* on sonochemical degradation rate is not obvious. The temperature theoretically produces two opposing mechanisms: on the one hand higher temperatures decrease the cavitation threshold by reducing surface tension and viscosity, promoting bubble growth, but on the other hand, higher vapour and gas content increase the resistance to the inward motion of a bubble during the collapse and decreases the polytropic index (ratio of heat capacities C_p/C_v) resulting in a reduced intensity of the collapse [25].
- Dosimeter factors (concentration): the dosimeter does not have any effect on the production of hydroxyl radicals. Nonetheless, its *concentration* might have an important effect over the trapping capacity of the $^\bullet$OH radicals. Higher concentrations should lead to an improved trapping capacity.
- Geometrical factors (volume and tip-bottom distance): the selected parameters were the *sample volume and the distance between the titanium horn tip and the bottom of the reactor*. The effect of the reactor design is more complex and mainly depends on the resonance phenomena of the propagating waves. Some authors have previously investigated such effect [26,27].

The selected response variable is the energy-specific $^\bullet$OH yield (*G* value), measured in mol of $^\bullet$OH radicals generated per joule. It is proportional to the generated $^\bullet$OH and to the scavenging capacity of the dosimeter. This parameter can be considered as a useful approximation of the efficiency of the process as an AOP.

4. Results and discussion

4.1. Salicylic acid dosimetry

The absorption spectra of the potential hydroxylation products, namely 2,3-dHBA, 2,4-dHBA, 2,5-dHBA, 2,6-dHBA and catechol, were obtained with the diode array detector and self-made standard solutions of these substances. Fig. 1 shows a typical chromatogram after 90 min of sonication, including the salicylic peak, the identified reaction products and the unidentified reaction products. Four different reaction product peaks were identified after the reaction (not taking into account the elution peaks). Peaks number 2, 3 and 4 appeared in every test, while peak number 1 was only identified in a few experiments. Peak 2 was identified as 2,5-dHBA with a 99.8% certainty (applying a qualitative comparison with the diode array spectrum obtained with the standard solution). Peak number 3 was identified with 99.9% certainty as 2,3-dHBA. Peak number 1 was not clearly identified as any of the other possible substances due to its low concentration. According to the retention times and to occasional interfering peaks, we cannot discard the possibility of obtaining marginal concentrations of 2,4-dHBA and 2,6-dHBA. Nevertheless, their concentration is considered to be almost negligible. Peak number 4 did not change its size during the experiments, and appeared even with zero sonication time,

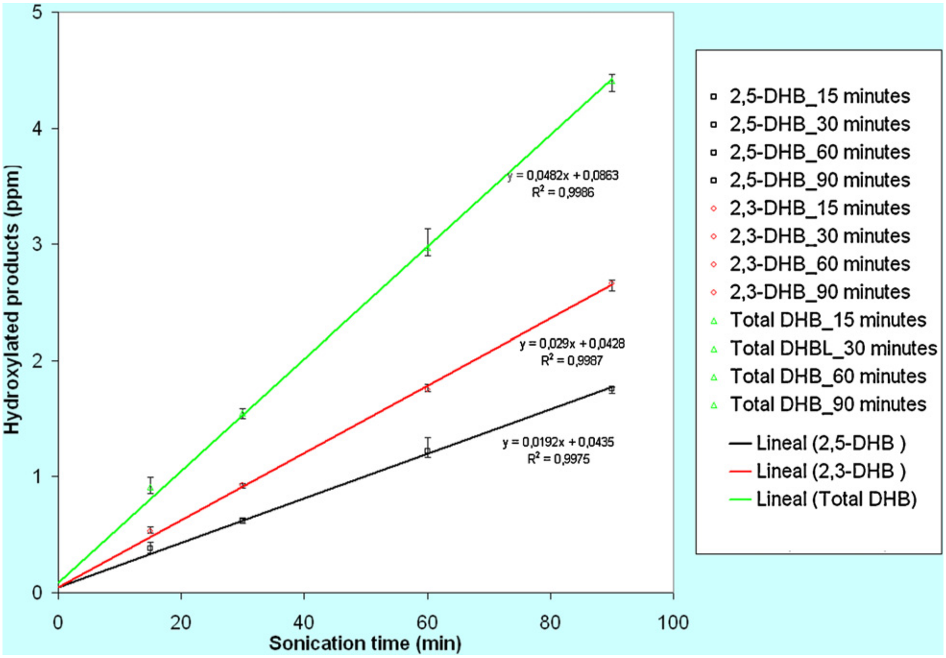

Fig. 2. Hydroxylated products generated during sonication. Conditions: sample volume 400 ml, initial salicylic acid concentration 200 mg/l, 20 °C ± 1, 70 W/cm^2 ± 4 and 28.1 mm distance horn tip-reactor bottom. Each value is the average of four times experiments and the error bar indicates maximal and minimum value.

which indicates that it might be caused by traces of contamination, either in the salicylic samples, in the column or in the reactor.

The concentration of $^\bullet$OH radicals is calculated considering that 1 mol of total detected hydroxylated products corresponds to 1 mol of $^\bullet$OH radicals produced in ultrasonic cavitation. Obviously, and despite all measures, it is impossible to guarantee that radicals are not recombining, reacting with other substances (scavengers) or that no other undetected substance is being produced. Neglecting these parallel processes implies that the number of detected $^\bullet$OH is lower than the actual $^\bullet$OH radicals being produced by the system, and so, the obtained results can be considered as a conservative approximation of the real $^\bullet$OH generation of the ultrasonic reactor. Fig. 2 shows the evolution of the identified hydroxylation products concentration with sonication time.

Taking into account the characteristic sizes of bubbles and the characteristic times of implosion in ultrasonic cavitation, the recombination of $^\bullet$OH radicals before reaching the liquid phase should be theoretically lower than in other cavitation processes, making appropriate the use of ionic dosimeters. Nevertheless, a comprehensive analysis of the influence of the solution pH was performed to determine the importance of $^\bullet$OH radicals recombination (by comparing the effectiveness of ionic salicylate in the liquid phase versus neutral salicylic in the gas–liquid interface). The result was that the reaction was accelerated by the migration of salicylic acid to the gas–liquid interface, keeping the pH constant below the pK_a of salicylic acid (2.97) [28].

4.2. Design of experiments

Two levels have been selected (see Table 1), constructing a 2-level factorial design with the aforementioned 5 parameters, that is a 2^5 factorial model (i.e. 32 experiments). The levels values were chosen so they would represent the most common experimental conditions according to previously published works. The experiments were performed using a random order, calculating the $G(^\bullet\text{OH})$ for each case (by summing up the energy-specific yield of the two main hydroxylated products).

Specific statistical software (Design Expert v. 7.0.0.) was used as the analytical tool for interpreting the results. This software provides highly efficient design of experiments (DOE) for identifying the effect of each parameter in the process. The first step is the diagnostic of the reliability of the selected model. The normal probability plot indicates whether the residuals follow a normal distribution or not. In normal distributions the points follow a straight line, indicating that the model can be selected for the analysis. Fig. 3(A) shows that initial data follow an inappropriate graphical adjustment. If the standard deviation associated with an observation is proportional to the mean raised to the power, then transforming the observation by the $1-\alpha$ (or λ) power gives a scale satisfying the equal variance requirement of the statistical model. The lambda value is related to a specific power law transformation function. By applying that transformation function to the data, and as shown in Fig. 3(B), the residuals adjust to a straight line, therefore indicating that the conclusions about the statistical importance of factors and their interactions in the experimental region will be correct [24].

Once the model has been validated, the results are analyzed in order to identify the significant factor effects. For that purpose, the program performs regression calculations to compute a table of effects for all model terms. The effects output can be shown as either a report or with graphical tools (Fig. 4). For 2-level factorial designs, the normal probability plot, shown in Fig. 4(A), represents the ordered values of a sample versus the expected ordered values from the true population. It will follow approximately a straight line. Thus, if the effects represent a sample from a normal population, it is expected to obtain a substantially straight line on a normal

Table 1
Selected parametrical range.

Factor	Lower value	Upper value
Sonochem. intensity [W/cm^2]	40	70
Initial concentration of scav. [mg/l]	50	200
Sample volume [ml]	200	400
Temperature [°C]	10	20
Distance tip-bottom [mm]	18.8	28.1

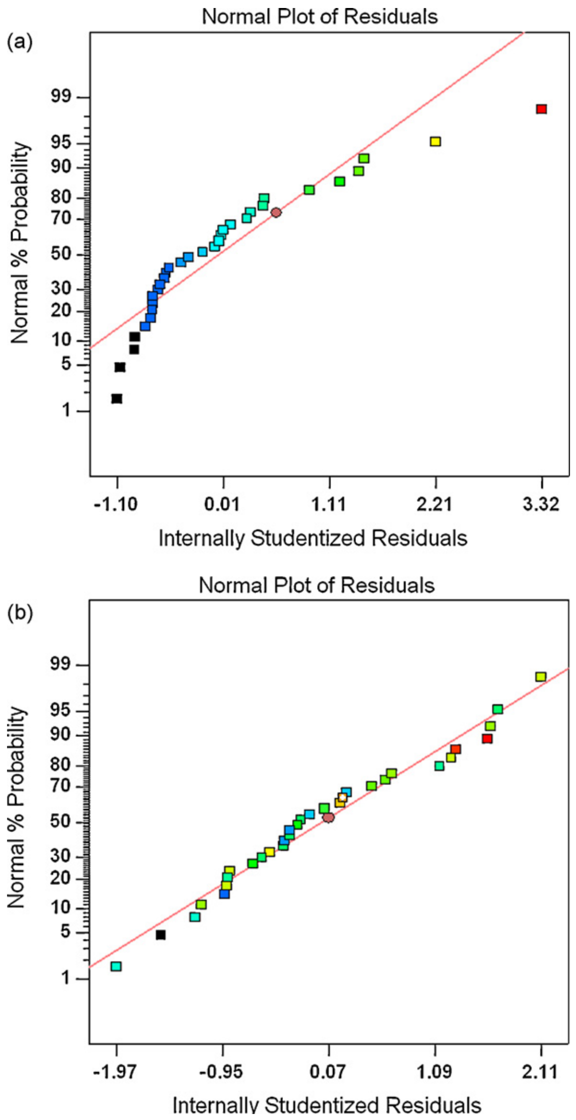

Fig. 3. Residuals data distribution with respect to the model internally calculated values, before (A) and after (B) applying transformation functions, respectively.

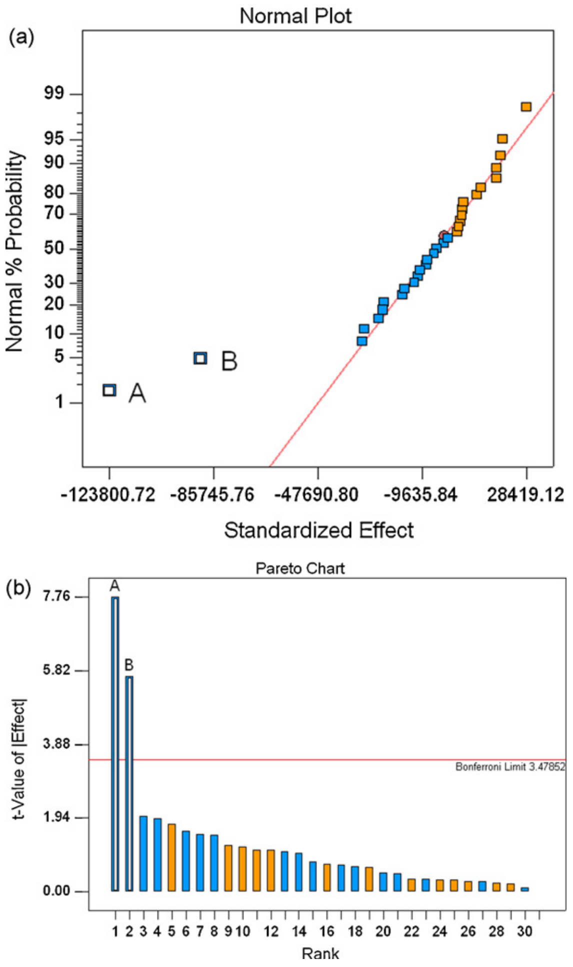

Fig. 4. Graphical outputs for analysing the significance of individual factors and its interaction on the selected response: (A) normal probability plot and (B) Pareto chart.

probability plot of the effects. The significant effects show up as outliers on the normal probability plot. The Pareto chart, shown in Fig. 4(B), is an additional graphic used to display the significance of the effects and its interactions. It is a histogram of frequencies where the length of each bar is proportional to the total effect value. The horizontal lines show the limits of statistical importance. Effects above the Bonferroni limit (line) are almost certainly significant.

Finally, the formal method to confirm these conclusions is the analysis of variance (ANOVA) where the values of significance (*p*-value) for the factors in the model are given. This parameter indicates the probability of seeing the measured value *F* (comparison of model variance with residual (error) variance) if the null hypothesis is true (no factor effect). A small probability implies that the null hypothesis is incorrect and that therefore the factor or the interaction is significant on the process.

The three aforementioned methods give up the same conclusions: the most significant factors of the process on the energy-specific $^{\bullet}$OH yield (*G* value), measured in mol of $^{\bullet}$OH radicals generated per joule, are the *sample volume* and the *initial concentration of scavenger* or dosimeter. The interaction between the factors does not seem to affect the results significantly. The rest of the factors do not have a significant effect within the studied range.

4.3. Significant parameters

As previously stated, the 2^5 factorial study is not broad enough to provide a general idea of the overall behaviour of sonochemical reactors. Such general conclusions would require at least a 3^6 factorial study (i.e. 729 experiments) and even then, there would be some factors and conditions which would have to be left out. Nonetheless, most standard reactors/conditions are accounted for in the 2^5 factorial study, and therefore the former analysis can be useful for comparison of many different experiments in the bibliography.

Theoretically, a larger *sample volume* should not have significant effects over the efficiency of the process, since the ultrasonic source and the sample conditions are not changed. Nevertheless, we have observed that this factor does have a significant effect over the process, and that a larger amount of liquid gives rise to higher efficiencies. There could be two main causes of this behaviour. First, under adequate agitation a larger volume provides a higher availability of scavenger (results indicate that the agitation caused by the sonicator is enough). But this cause alone does not entirely explain the observed improvement. The only parameter which changes together with the volume is the distance from the surface to the tip. The effect of this change might be an additional cause of the observed behaviour. Obviously this does not mean that increasing the amount of liquid would always cause higher efficiencies, but it might be a warning against comparisons between experiments with different sample volumes, or more generally, against the comparison between reactors with different geometry.

On the other hand, the *initial concentration* of scavenger is the most significant factor on the degradation of salicylic acid. As previously mentioned, this factor is directly related to the trapping capacity of the scavenger but not to an increase of the $^{\bullet}$OH generation in the system. Ideally, all hydroxyl radicals generated in the system would react with the dosimeter, and consequently no changes would be observed when using different substrate concentration. Results indicate that the trapping efficiency of the dosimeter is much more significant than any other parameter. This observation is a warning against comparisons results obtained with different dosimeters and/or scavenger concentrations. This might also explain the significant differences observed by the authors when comparing results of $^{\bullet}$OH measurements using different dosimeters [21].

The rest of the parameters, namely *temperature*, *intensity* and *distance of the tip* have demonstrated to have a lower significance in the process, at least in the selected range. Of course, it must be taken into account that the selected operation range was intended to represent the most common operation conditions in 20 kHz reactors, leaving out extreme conditions which would have given very different results (i.e. a 3^n factorial study would allow using an intermediate value plus a high and a low value (extremes), accounting for the overall effects of each parameter). In fact, some additional experiments were performed using very low intensities (5 W/cm^2) or destructive tip-bottom distances ($\lambda/2$ mm), which resulted in merely traces of the hydroxylated substances, which demonstrated that these factors do have an important effect when operating in wider ranges.

5. Conclusions

The salicylic acid dosimetry has demonstrated to be a reliable standard method for the indirect determination of hydroxyl radicals in a biphasic aqueous solution (i.e. cavitating system) and for testing the performance of sonochemical equipments.

The reaction of salicylic acid with the $^{\bullet}$OH radicals gives rise to specific hydroxylated products (mainly 2,3-DHB and 2,5-DHB). Due to its hydrophobicity at low pH values, the reaction takes place in the gas–liquid interface, avoiding excessive recombination and undesired scavenging of $^{\bullet}$OH during the diffusion to the liquid-phase.

Statistical methods are useful for both, designing set of experiments, and managing the final results. These tools provide a mathematical background to the conclusions which is essential to construct a solid ground in the optimization of the sonochemical technology. A 2^5 factorial set of experiments was designed using DOE software and the 2 levels of each of the 5 selected parameters were defined trying to cover the most usual experimental conditions found in the bibliography. In general, the effects of individual factors follow the theoretical expectations, except for sample volume and distance between titanium horn tip and the bottom of the reactor. Nevertheless, within the selected range, only the reaction volume and the concentration of scavenger had a significant effect over the results. No significant interdependences were observed in the studied range.

According to the results, when operating within a standard working range (i.e. within the ranges defined in this study), only the aforementioned variables have a mathematical significance on the efficiency of the process. This indicates that when comparing or reproducing experimental results, it is critical that the authors take into account the concentration of substrate (either dosimeter or pollutant) and the liquid volume (or the reactor geometry). In fact, some of the differences observed in apparently similar processes/reactors could by explained by relatively small changes in either of these factors.

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References

[1] T.J. Mason, Sonochemistry, Oxford Science Publications, New York, 1999, pp. 1–47.
[2] K.S. Suslick, Sonochemistry, Science 247 (1990) 1439–1445.
[3] K.S. Suslick, D.A. Hammerton, R.E. Cline, The sonochemical hot spot, J. Am. Chem. Soc. 108 (1986) 5641–5642.
[4] T.J. Mason, J.P. Lorimer, Applied Sonochemistry, Wiley-VCH, 2002.
[5] A. Behnajady Mohammad, N. Modirshahla, M. Shokri, V. Behrouz, Effect of operational parameters on degradation of malachite green by ultrasonic irradiation, Ultrason. Sonochem. 15 (2008) 1009–1014.
[6] A. Henglein, Chemical effects of continuous and pulsed ultrasound in aqueous solutions, Ultrason. Sonochem. 2 (1995) 115–121.
[7] J.Z. Sostaric, A comparative sonochemical reaction that is independent of the intensity of ultrasound and the geometry of the exposure apparatus, Ultrason. Sonochem. 15 (2008) 1043–1048.
[8] R.A. Torres, C. Petrier, E. Combet, M. Carrier, C. Pulgarin, Ultrasonic cavitation applied to the treatment of bisphenol-A. Effect of sonochemical parameters and analysis of BPA by-products, Ultrason. Sonochem. 15 (2008) 605–611.
[9] G. Mark, A. Tauber, R. Laupert, H.-P. Schuchmann, D. Schulz, A. Mues, C.V. Sonntag, OH-radical formation by ultrasound in aqueous solution. Part II. Terephthalate and Fricke dosimetry and the influence of various conditions on the sonolytic yield, Ultrason. Sonochem. 5 (1998) 41–52.
[10] G. Isil, N.H. Ince, Ultrasonic destruction of bisphenol-A: the operating parameters, Ultrason. Sonochem. 15 (2008) 524–529.
[11] H.E. Mohammad, T.R. Bastami, Influence of ultrasound on cadmium ion removal by sorption process, Ultrason. Sonochem. 15 (2008) 428–432.
[12] J. Klíma, A. Frias-Ferrer, J. González-García, J. Ludvík, V. Sáez, J. Iniesta, Optimisation of 20 kHz sonoreactor geometry on the basis of numerical simulation of local ultrasonic intensity and qualitative comparison with experimental results, Ultrason. Sonochem. 14 (2007) 19–28.
[13] C. Nikitenko Le Naour, P. Moisy, Comparative study of sonochemical reactors with different geometry using thermal and chemical probes, Ultrason. Sonochem. 14 (2007) 330–336.
[14] Y. Benito, S. Arrojo, G. Hauke, P. Vidal, Hydrodynamic cavitation as a low-cost AOP for wastewater treatment: preliminary results and a new design approach, in: Water Resources Management III, Wessex Institute of Technology, 2005, pp. 495–504.
[15] Y. Iida, K. Yasui, T. Tuziuti, M. Sivakumar, Sonochemistry and its dosimetry, Microchem. J. 2 (2005) 159–164.
[16] A.K. Jana, S.N. Chatterjee, Estimation of hydroxyl free radicals produced by ultrasound in Fricke solution used as a chemical dosimeter, Ultrason. Sonochem. 2 (1995) 87–91.
[17] P.R. Gogate, A. Pandit, Cavitation reactors: efficiency assessment using a model reaction, AIChE J. 47 (11) (2001) 2526–2537.
[18] X. Fang, G. Mark, C. von Sonntag, OH radical formation by ultrasound in aqueous solutions. Part I. The chemistry underlying the terephthalate dosimeter, Ultrason. Sonochem. 3 (1996) 57–63.
[19] T.J. Mason, J.P. Lorimer, D.M. Bates, Y. Zhao, Dosimetry in sonochemistry: the use of aqueous terephthalate ion as a fluorescence monitor, Ultrason. Sonochem. 1 (2) (1994) 91–95.
[20] G.J. Price, E.J. Lenz, The use of dosimeters to measure radical production in aqueous sonochemical systems, Ultrasonics 31 (1993) 451–456.
[21] S. Arrojo, C. Nerín, Y. Benito, Application of salicylic acid dosimetry to evaluate hydrodynamic cavitation as an advanced oxidation process, Ultrason. Sonochem. 14 (2007) 343–349.
[22] J.-F. Jen, M.-F. Leu, T.C. Yang, Determination of hydroxyl radicals in an advanced oxidation process with salicylic acid trapping and liquid chromatography, J. Chromatogr. A 796 (1998) 283–288.
[23] A.G. Chakinala, P.R. Gogate, A.E. Burgess, D.H. Bremner, Intensification of hydroxyl radical production in sonochemical reactors, Ultrason. Sonochem. 14 (2007) 509–514.
[24] D.C. Montgomery, Design and Analysis of Experiments, Arizona State University, Editorial Wiley, 2005.
[25] K. Gaddam, H. Michael Cheung, Effects of pressure, temperature, and pH on the sonochemical destruction of 1,1,1-trichloroethane in dilute aqueous solution, Ultrason. Sonochem. 8 (2001) 103–109.

[26] M. Goel, H. Hongqiang, A.S. Mujumdar, M.B. Ray, Sonochemical decomposition of volatile and non-volatile organic compounds—a comparative study, Water Res. 38 (2004) 4247–4261.

[27] K. Yasui, T. Kozuka, T. Tuziuti, A. Towata, Y. Iida, J. King, P. Macey, FEM calculation of an acoustic field in a sonochemical reactor, Ultrason. Sonochem. 14 (2007) 605–614.

[28] G.V. Ambulgekar, S.D. Samant, A.B. Pandit, Oxidation of alkylarenes using aqueous potassium permanganate under cavitation: comparison of acoustic and hydrodynamic techniques, Ultrason. Sonochem. 12 (2005) 85–90.