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Optimization of a Hydrodynamic Cavitation Reactor using Salicylic acid Dosimetry

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Abstract

In the present work, optimization of a hydrodynamic cavitation reactor, for maximizing the extent of hydroxyl radical generation, has been investigated using salicylic acid as a dosimeter. The effect of differing operating parameters such as inlet pressure into the reactor, shape of the orifice, and concentration of salicylic acid employed was investigated where the extent of hydroxyl radical generation was quantified in terms of concentration of the hydroxylated products 2,5- and 2,3- dihydroxybenzoic acid. With an upstream pressure of <100 psi no hydroxyl radicals were produced but excellent results were obtained with a small circular nozzle at 4000 psi and a salicylate concentration of 750 ppm. The use of a combination of ultrasound along with hydrodynamic cavitation is also reported for the first time and results in a 15% improvement in the hydroxyl radical generation when the distance between the orifice and transducer is 5 mm to 10 mm.

Keywords: Hydrodynamic cavitation, salicylic acid dosimetry, hydroxyl radicals, ultrasonic cavitation, optimization

1. Introduction

Cavitation reactors find a widespread application in the areas of chemical processing, water and effluent treatment, biotechnology, polymer chemistry, solid-liquid extraction, crystallization and the petroleum and textile industries [1-2]. Among the different available modes of generation of cavitation viz. acoustic, hydrodynamic, laser and particle, only acoustic and hydrodynamic cavitation produce intensities suitable for any physical or chemical processing applications [3-4]. While acoustic cavitation has been predominantly investigated over the years [5-10], hydrodynamic cavitation, where the cavities are generated due to alteration of the flow conditions and subjected to turbulent pressure field oscillations, has been a comparatively recent advent [11-12] and has been shown to be more energy efficient as compared to the sonochemical reactors for applications such as microbial cell disruption [13,14], wastewater treatment [15-17] and chemical synthesis [18,19]. To give a quantitative idea, Ambulgekar et al. [18] have reported that the cavitation yield (defined as yield of product per unit supplied electrical energy) for the synthesis of benzoic acid was 2.7×10^{-5} mol/kJ using hydrodynamic cavitation whereas for acoustic cavitation it was 4.63×10^{-6} mol/kJ. Kelkar et al. [19] have also reported that depending on the type of acid/alcohol combination used for the synthesis of biodiesel, the yields per unit energy for hydrodynamic cavitation varied in the range of 1×10^{-4} – 2×10^{-4} g/J (on the basis of supplied energy) whereas for acoustic cavitation it was order of magnitude lower, i.e., in the range of 5×10^{-6} – 2×10^{-5} g/J.

One of the main limitations of hydrodynamic cavitation reactors has been in terms of intensity of cavitation generated in the system, which is often low compared to the acoustic cavitation based reactors. With this background in mind, the present work reports an investigation into optimization of different operating and geometric parameters and also use of a combination of hydrodynamic and ultrasonic cavitation in the same reactor. The

ultrasonic flow cell was used downstream of the orifice chamber which allowed the collapse of the cavities, which are generated due to the presence of orifice, under the influence of the ultrasound pressure field. The effect of distance between the orifice and the ultrasonic flow cell was also investigated. The implications of the obtained results can be for wastewater treatment applications or for chemical synthesis where controlling mechanism is based on free radical attack.

Salicylic acid dosimetry has been used as a measure of quantifying the efficacy of cavitation reactors for hydroxyl radical production. The dosimetry based on salicylic acid is very specific, meaning that the reaction products are exclusively caused by the hydroxyl radical oxidation reaction, usually addition of the hydroxyl radical to the aromatic ring. The reaction products of salicylic acid dosimetry can be determined using HPLC with greater sensitivity than the spectrophotometric measurements used with iodide and Fricke dosimeter [20]. Also, it has been reported recently that the iodide oxidation reaction may not give true measures of cavitation activity especially in hydrodynamic cavitation reactors, as it is observed that even without cavitation, iodide was consumed at a rapid rate leading to an equilibrium concentration [21].

2. Materials and Methods:

2.1 Materials:

Experiments were carried out in a hydrodynamic cavitation reactor (hydrocavitator) depicted schematically in Figure 1. The reactor was connected to a three cylinder triplex pump (NP25/21-350; Speck Pumps (UK) Ltd.) for continuous recirculation of the liquid. Nozzles (Spraying Systems Company, UK and Lechler Ltd UK) with different geometries (Table 1) were used to investigate the effect of hydroxyl radical production within the cavitation chamber. The pump used for production of the hydrodynamic cavitation has rated

power consumption of 14.8 kW and the actual operation was done at a loading of 15% indicating that the supplied power to the reactor was 2.22 kW. In experiments with a combination of ultrasonic and acoustic cavitation, an ultrasonic probe was placed on the downstream side of the nozzle so as to achieve collapse of the cavities under the influence of ultrasonic pressure field. The ultrasonic probe (Sonics and Materials Inc), fitted with a 1 cm replaceable tip, is capable of operating continuously or in a pulse mode at a fixed frequency of 20 kHz. The ultrasound was produced by a unit having a rated power of 600 watts and the actual operation was at 70% loading (420 W was the supplied power).

Salicylic acid (Reagent Plus grade with purity greater than 99 %) was procured from Sigma-Aldrich, Dorset UK and was used as received. The aqueous solution of salicylic acid was prepared by dissolving salicylic acid in de-ionized water to make appropriate concentrations of 250, 500, 750 and 1500 ppm.

2.2 Experimental procedure

The stainless steel hydrocavitator was washed with large volumes of tap water to remove any residue and chemicals in the setup before each experiment. The total volume of salicylic acid solution in water used for the experiments was 4L. The effect of upstream pressure on the extent of hydroxyl radical generation was investigated over the range of 100 psi to 4000 psi (maximum possible pressure with the given setup was 4000 psi) and the concentration of salicylic acid studied was varied between 250 ppm and 1500 ppm.

In the combination studies, the effect of distance between the cavitation chamber generating hydrodynamic cavitation and the ultrasonic probe, where collapse takes place, was investigated over the range of 5 mm to 30 mm. Different types of nozzles (table 1) were also used in the work with the objective of investigating the effect of the design of the cavitation generating device.

All the experiments were performed in duplicate and experimental errors were always less than $\pm 2\%$ of the obtained value.

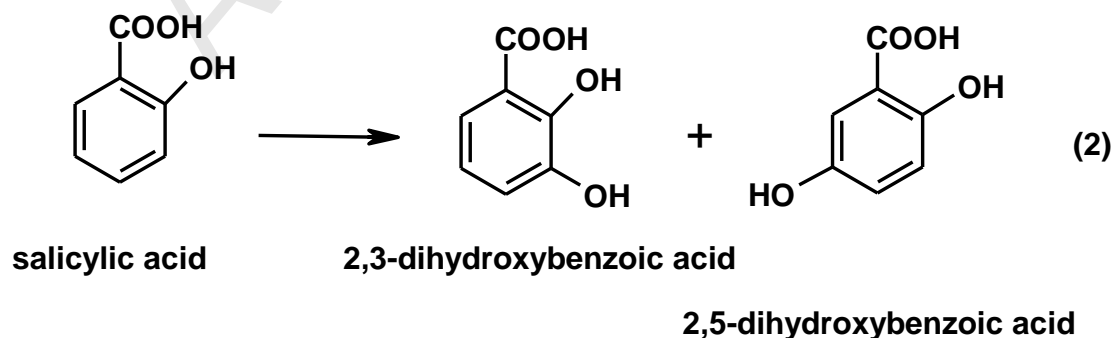
2.3 Analysis

Samples, collected every 10 minutes, were analysed using High Performance Liquid Chromatography (HPLC; Waters) consisting of an in-line degasser, a binary HPLC Pump, a dual λ absorbance detector, an autosampler and a reverse phase C₁₈ Partisil 5 ODS 3- μ Bondapak (250 x 4.6 mm, 5 μ) column. The mobile phase used was 60:40 ratio of phosphoric acid (prepared by adding 1.36 mL of orthophosphoric acid to 1000 mL of distilled water) and HPLC grade methanol. The mobile phase flow rate was 1 mL/min and the injection volume was 20 μ L with a total analysis run time of 20 min.

3. Results and Discussions:

3.1 Effect of salicylic acid concentration:

When water is subjected to hydrodynamic cavitation the hydrogen to oxygen bond is ruptured resulting in the formation of a hydroxyl radical and a hydrogen atom (Equation 1). In the presence of salicylic acid the hydroxyl radical is trapped forming both 2,3-dihydroxybenzoic acid and 2,5-dihydroxybenzoic acid (Equation 2).



The effect of initial concentration of salicylic acid solution used in the reactor on the extent of trapping of hydroxyl radicals from water was investigated by varying the salicylic acid concentrations over a range of 250 ppm to 1500 ppm. Figure 2 clearly shows that the maximum product formation (2,3-dihydroxybenzoic acid + 2,5-dihydroxybenzoic acid) and hence the most efficient hydroxyl radical trapping concentration is observed at an initial concentration of 750 ppm. The observed results can be attributed to the competition equilibrium established between the salicylic acid and the primary derivatives for trapping the generated hydroxyl radicals in the system. It should be also noted that the rate of generation of hydroxyl radicals (e.g. using a cavitation reactor, a Fenton chemistry mechanism or a photocatalytic oxidation reactor) also decides the optimum value of the salicylic acid concentration. Jen et al. [22], with experiments for hydroxyl radical generation using Fenton chemistry mechanism, have shown that optimum concentration of salicylic acid is 250 ppm beyond which the total product formation is constant. Consequently, the experiments related to the effect of other operating parameters in the present work were all performed at an initial concentration of 750 ppm salicylic acid.

3.2 Effect of Upstream Pressure:

The effect of upstream pressure on the hydroxyl radical production in the reactor was studied by applying high pressure to the inlet salicylic acid solution over the range of < 100 psi to 4000 psi. The nozzle F which had the smallest orifice area so that the maximum pressure could be attained in the system was used for these studies. It can be seen in figure 3 that higher upstream pressure resulted in an increase in the extent of hydroxyl radical production as indicated by the concentration of the hydroxylated products of salicylic acid measured. It has been also observed that absolutely no product formation can be seen at pressures below 100 psi indicating that a minimum pressure is required for onset of cavitation events and

subsequent release of the free radicals. Shirgaonkar et al. [23] have also reported a similar existence of critical operating pressure in a high pressure homogenizer with experiments on iodine release and microbial cell disruption. Kumar and Pandit [24] observed comparable results based on the theoretical studies of bubble dynamics analysis and experimental investigations based on decomposition of potassium iodide in a high speed homogenizer. The observed increase in the product formation with higher inlet pressure beyond the critical operating pressure for onset of cavitation effects can be attributed to a bigger pressure drop across the orifice resulting in an increase in the collapse intensity of the cavities [25] which results in enhanced local pressures and temperatures resulting in more hydroxyl radicals being generated in the system. Evidence to elevated cavitation activity at higher inlet pressures can be also obtained from experimentally observed superior cavitation effects for different applications such as degradation of pollutants in industrial wastewater [26], oxidation of potassium iodide [27] and cell disruption [28].

3.3 Effect of the shape of the constriction:

The constriction (a nozzle in the present case) is the main operating device which decides the extent of cavitation intensity generated and hence the amount of hydroxyl radicals produced. In the present work, the effect of five nozzles differing in the shape and flow area were investigated (Table 1) and the results are depicted in Figure 4. It can be seen from the figure that nozzle B, which has maximum flow area (circular shape with 1.09 mm diameter) generates the lowest concentration of free radicals, as indicated by the lowest yield of products. Nozzles A and H have a virtually identical profile, though after some time (40 min) nozzle A seems to generate marginally more intense cavitation. The difference can be attributed to higher shear layer area offered by the elliptical nozzle as compared to the rectangular shape of the nozzle, though the flow area for both the nozzles is identical.

Vichare et al. [27] have reported similar effects of the shear layer area for different nozzles with same flow area. The most efficient nozzle was found to be F which also has the smallest diameter of hole, followed by Nozzle G (circular in shape with 0.9mm diameter). The dependency of the yield of the product and hence the efficacy for hydroxyl generation can be attributed to the different cavitation intensity generated for nozzles with varying flow area. Gogate and Pandit [25] have shown that the cavitation intensity, quantified in terms of the pressure pulse generated due to the collapse of the cavities, decreased with an increase in the flow area. Vichare et al. [27] have also reported similar results for experiments with KI oxidation as model reaction.

3.4 Effect of combination of ultrasound and hydrodynamic cavitation:

Figure 5 shows the effect of the presence of ultrasound on the extent of hydroxyl radical production at an operating pressure of 4000 psi (nozzle H). It can be seen that use of ultrasound in combination with hydrodynamic cavitation results in about a 15% increase in the extent of hydroxyl radical generation as indicated by enhanced production of the hydroxylated products. Similar results have been reported in experiments on water disinfection [28], however, the extent of increase in the extent of water disinfection is much larger as compared to that obtained in the present work (around 3 times more). The variation was attributed to much lower operating pressures, which indicates that the extent of cavitation intensity generated by hydrodynamic means is low and hence the presence of ultrasonic irradiation is proportionally much more effective.

The effect of distance between the nozzle and the ultrasonic probe in the reactor was also investigated by varying the distance from 5 mm to 30 mm and the obtained data has been given in Table 2. As can be seen from the table the extent of hydroxyl radical production marginally increases with distance from 5 mm to 10 mm but then shows a decrease (going

from 20mm to 30 mm) in the cavitation intensity and hence the extent of free radical generation. This is probably due to the dependency of the phase of cavity on the distance from the point of generation. In a typical transient cavitation event, the generated cavity grows to a maximum and then instantaneously collapses generating free radicals. At the optimum distance observed in the present work, it is likely that when the cavity reaches the influence of ultrasonic irradiation, it is approaching the maximum growth phase and the complete collapse is under the influence of ultrasound giving enhanced hydroxyl radical production. While the exact mechanism of the increase in the extent of free radical generation still cannot be fully explained, the present work has clearly established the fact that the combination of ultrasound and hydrodynamic cavitation can be used beneficially for chemical processing applications which are controlled by a free radical mechanism.

4. Conclusions:

Salicylic acid dosimetry has been used effectively to quantify the hydroxyl radical generation in a hydrodynamic cavitation reactor and the following important design related information can be established based on the findings of the present work:

1. An optimum concentration of salicylic acid is recommended based on the specific method for hydroxyl radical production since the rate of trapping of the radicals would be maximal at an optimum loading of salicylic acid.
2. A critical operating pressure exists for generation of significant intensity cavitation to bring about desired chemical processing applications; beyond this value an increase in the operating pressure (up to a maximum of 4000 psi used in this study) is beneficial.
3. The nozzle with the least flow area (orifice F in the present case) was the most effective at hydroxyl radical production. For an orifice with similar flow area, the one with the larger shear layer area was found to be more effective.

4. The use of a combination of ultrasound along with hydrodynamic cavitation results in a marginal improvement in the hydroxyl radical generation and an optimum distance also exists where maximum benefit is obtained. The obtained effects are also dependent on the operating pressures and it is recommended that further work is carried out on the design of the dual cavitation reactor for selection of the most efficient combination strategy.

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Figure 6: Effect of distance between ultrasound source and hydrodynamic cavitation on the extent of hydroxyl radical production as measured by dihydroxybenzoic acid formation (mM)

Orifice	Supplier	Dimensions	Shape
A	Spraying Systems	0.4mm x 0.25mm	Elliptical
B	Lechler	1.09mm diameter	Circular
F	Lechler	0.6mm	Circular
G	Lechler	0.9mm	Circular
H	Spraying Systems	0.4mm x 0.2mm	Rectangular

Table 1: Characteristics of the orifices

Time of Operation	Product Concentration (mM)			
	Distance = 5 mm	Distance= 10 mm	Distance = 20 mm	Distance = 30 mm
10	0.54	0.69	0.62	0.7
20	1.09	1.29	1.23	1.31
30	1.99	2.11	2.1	2.14
40	2.89	2.97	2.99	2.86
50	3.73	3.8	3.7	3.64

Table 2: Effect of distance between the ultrasonic probe and hydrodynamic cavitation reactor on the extent of free radical generation

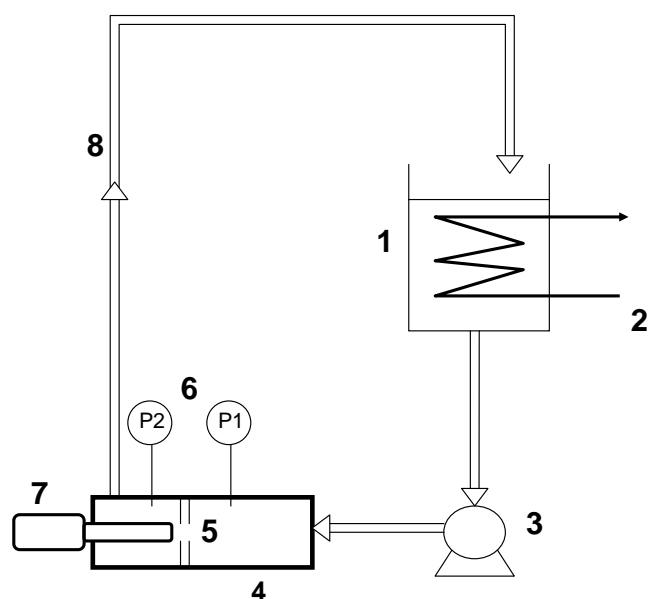


Figure 1: Schematic representation of the hydrodynamic cavitation/ultrasound reactor
1, Feeder tank; 2, cooling coil; 3, high pressure pump; 4, orifice unit; 5, orifice; 6, pressure gauges; 7, ultrasonic transducer unit; 8, return pipe.

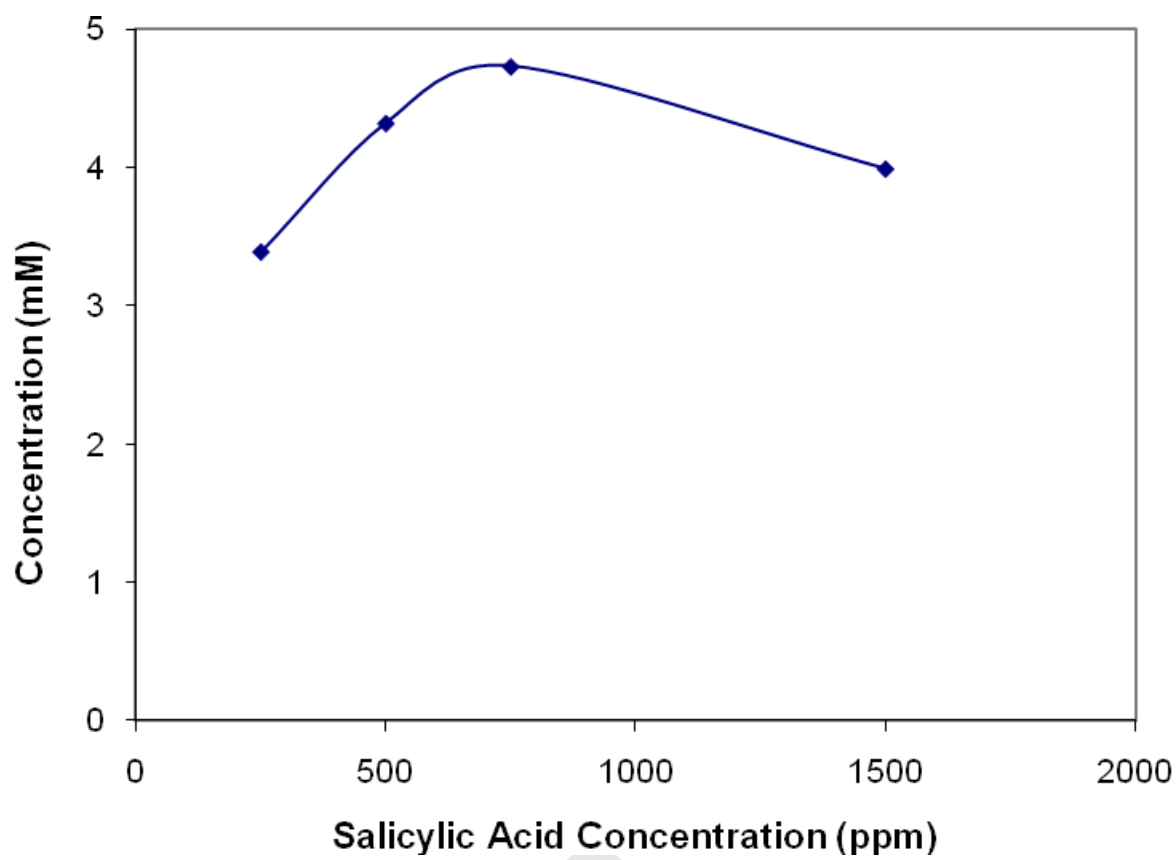


Figure 2: Effect of concentration of salicylic acid on the extent of hydroxyl radical trapping

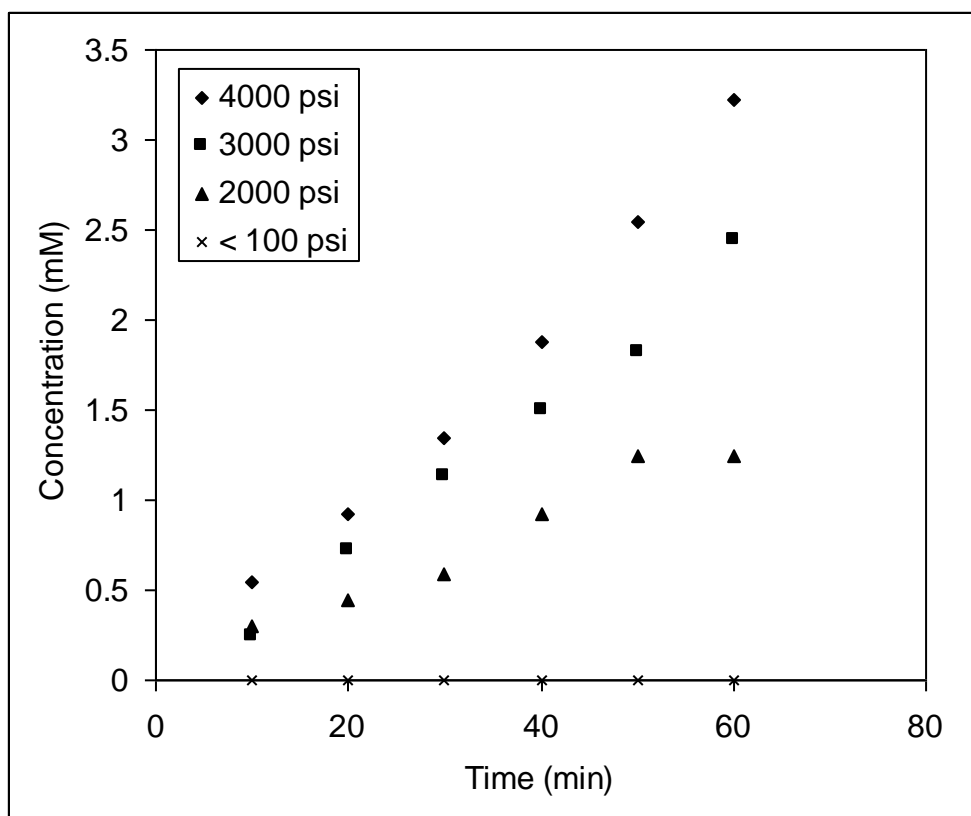


Figure 3 Effect of upstream pressure on the extent of hydroxyl radical production as measured by dihydroxybenzoic acid formation (mM).

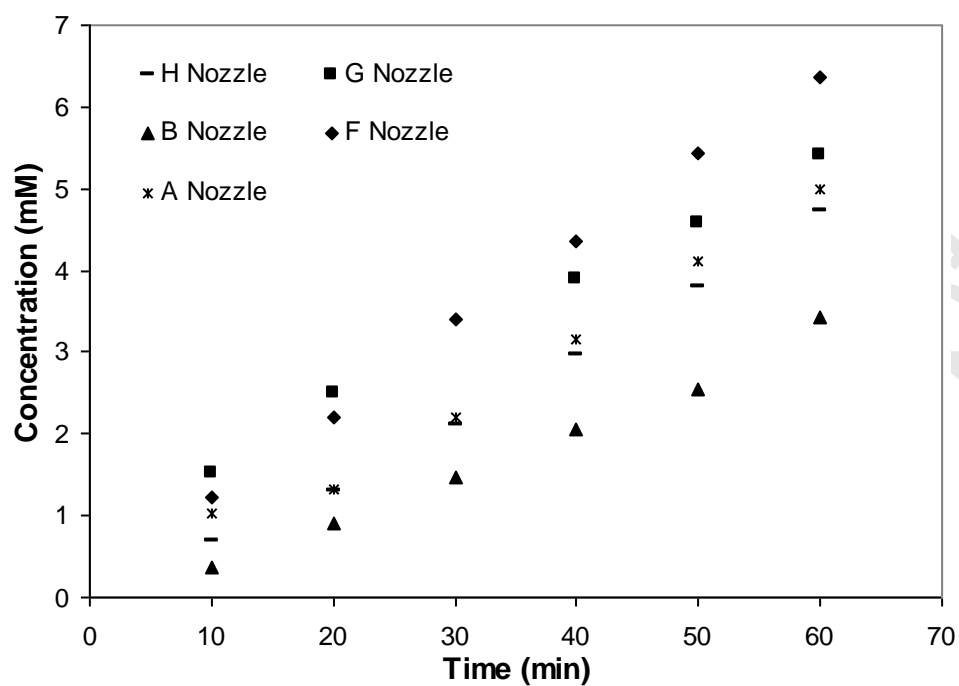


Figure 4 Effect of different nozzles on the extent of hydroxyl radical production as measured by dihydroxybenzoic acid formation (mM)

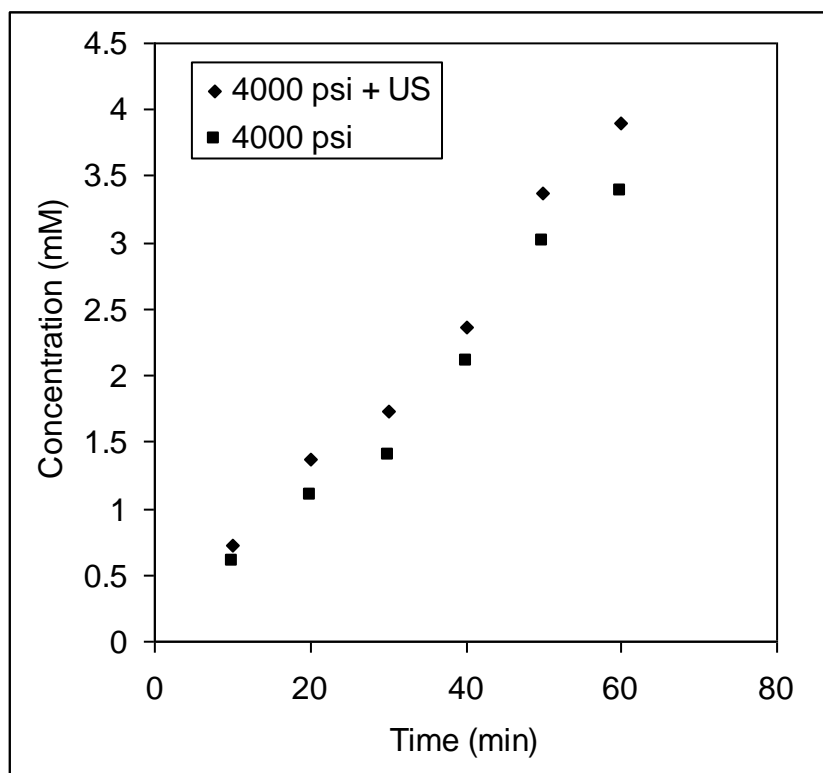


Figure 5 Effect of presence of ultrasonic irradiation on the extent of hydroxyl radical production as measured by dihydroxybenzoic acid formation (mM)