CHEMICAL ENGINEERING TRANSACTIONS
VOL. 32, 2013
A publication of AIDIC
The Italian Association of Chemical Engineering
Online at: www.aidic.it/cet
Chief Editors: Sauro Pierucci, Jiří J. Klemeš

ISBN 978-88-95608-23-5; **ISSN** 1974-9791
DOI: 10.3303/CET1332116

Understanding the Physics of Advanced Oxidation in a Venturi Reactor

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This paper is part of a research activity concerning theoretical and experimental studies of cavitation as an Advanced Oxidation Process in a convergent-divergent nozzle. The capability and peculiarities of this technology in degrading organic pollutants in water effluents are addressed by theoretical and experimental studies. Dosimetry methods for estimation of hydroxyl radical production are carried out through p-nitrophenol degradation. Additionally, for investigating the phenomenology of Venturi oxidation, a mathematical algorithm is proposed, which couples a microscopic approach (on single bubble dynamic with chemical reactions) with a macroscopic one (nucleation of bubbles' clouds). Experimental evidences agree with numerical ones in identifying an optimum level of inlet fluid pressure, in producing the highest experimental removal rate and the highest theoretical radicals' production.

1. Introduction

The increasing requirements of human beings are strictly related to the growing impact of industrial effluent on wastewater discharges and to the presence of new substances in aquatic environments, not degraded by conventional treatments. The fulfilment of severe water quality standards with respect to those pollutants, leads to the development of innovative technologies to solve the problem of tertiary treatment (Eusebi et. al., 2011), *e.g.* advanced oxidation (AOPs) process schemes in which hydroxyl radicals generation occurs, to oxidize many of the complex chemicals present in the effluent water (Rosa et al., 2012). Among these techniques, cavitation has been widely investigated for wastewater treatment applications, particularly regarding ultrasonically induced cavitation (Capocelli et al., 2012). Although the latter has showed promising results on lab scale, it is not energy-efficient and presents some technical issues on large scale applications (Gogate et al., 2011). In this framework, hydrodynamic cavitation has been recognized as a cost-effective alternative thanks to its low power consumption and simplicity of construction and maintenance (Gogate and Pandit, 2004).
The efficiency of hydrodynamic cavitation is the result of several parameters such as the number of actual cavitational events, the residence time of cavities in the low-pressure zone and the rate of pressure recovery (Sharma et al., 2008). The cited factors depend on the hydraulic characteristics as well as on the geometrical configuration of Venturi nozzle, which can be considered as a chemical reactor. Although the phenomenology of cavitation is well known, there is still the need to establish correlations and to obtain practical and quantitative information in the field of reactor design, with the goal of definitely turning the application into a consolidated waste-water treatment (Capocelli et al., 2012, 2013). Additionally, the influence of bubble dynamics and transport mechanisms on the oxidation kinetic regime (Karatza et al., 2008, 2010) is still a unexplored field of research.
In the current work, the optimization of the influent parameters and the understanding of their effects are dealt with, based on experimental and theoretical studies. The approach of coupling experimental campaign with theoretical models (which consider the related phenomena, such as chemical kinetics,

Please cite this article as: Capocelli M., Prisciandaro M., Musmarra D., Lancia A., 2013, Understanding the physics of advanced oxidation in a venturi reactor, Chemical Engineering Transactions, 32, 691-696 DOI: 10.3303/CET1332116

bubble population and transport phenomena) would allow designers and engineers to gain insight into the physics and improve their predicting skills.

2. Experimental apparatus and Methodologies

A schematic of the experimental setup used for hydrodynamic cavitation is shown in Figure 1. The setup essentially consists of a closed loop circuit including a holding tank of capacity 1.5 L (with a cooling jacket in order to keep the solution temperature at 30°C), a bypass line equipped with a needle valve, used to regulate pressure and flow-rate at the constriction, and a centrifugal pump (max 3500 rpm) of maximum power rating 400 W. The convergent-divergent nozzle has the dimension d_p = 12 mm; d_o = 2 mm; l_1 = 20 mm; l_2 = 12 mm; l_3 = 50 mm. Additionally, in Figure 1, the main operative parameters (flow-rate q; inlet pressure P_1 and recovered pressure P_2) are highlighted.
Radical production (dosimetry method) was estimated by observing p-nitrophenol degradation. The initial concentration of p-nitrophenol was 1 mg/L, the pH of solution 5 and the concentration was monitored at the spectrophotometer at λ=401nm (Kotronarau et al.,1991). For investigating the hydrodynamic influence on degradation kinetics, the inlet pressure P_1 was varied in the range 2-6 bar, by varying the flow in the bypass line. The flow rate through the Venturi changes as a function of P_1 values: from 3.46 L/min (at 2 bar) to 5.99 L/min (at 6 bar).

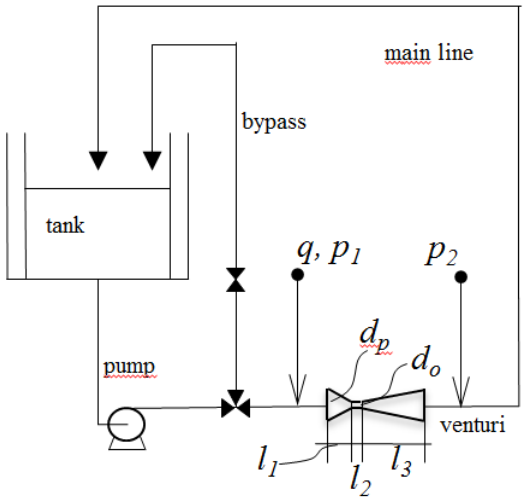

Figure 1:Schematic representation of the experimental apparatus

3. Mathematical Algorithm

The algorithm described in this section aims at simulating the bubble dynamics and the hydroxyl radical production in a Venturi reactor. The geometrical dimensions are set according to the value of the experimental apparatus (parameter $\beta = d_p/d_o$ is variable) and the inlet pressure and flow-rate are varied in the experimental range. The model of bubble dynamics used for the following simulation is based on the considerations put forward in a seminal paper by Toegel et al. in 2000. It consists of the Keller and Miksis equation for bubble dynamics, the mass balance with the diffusion limited approach and chemical reactions, the energy balance on the bubble as described in several papers (Capocelli et al., 2012, 2013; Khrishnan et al., 2006). In writing the ODEs system for the cavitating flow in such geometries, we adopt the approach of Moholkar and Pandit (1997), based on the assumption of steady state cavitating flow for a constant mass flow rate. This approach is the basis of several numerical studies of the last years and allows the estimation of the theoretical availability of hydroxyl radicals at the collapse stage of a bubble. The algorithm implemented in this work is illustrated in Figure 2. The upper part points out the solution of the single bubble dynamic equation and the chemical reactions at the collapse stage in order to quantify the radical •OH production for each bubble and it is based on consolidated theoretical works (see the cited papers for further details). The main input parameters are the pressure profile (dependent on the geometrical configuration) and the flow rate. For modelling the local bulk liquid pressure, which directly influences bubble nucleation, growth and collapse, the algorithm of Moholkar and Pandit (1997) was used. Thus, the instantaneous velocity in the flow downstream of the orifice (useful for the calculation of the

pressure profile) can be written as the sum of two contributions: the mean flow velocity and the turbulent fluctuating velocity in the axial direction.
The lower part of Figure 2 shows the novelty introduced in the current study: a global approach that takes into account the simultaneous presence of an actual multitude of bubbles. As reported in Eq.(1), the hydroxyl radical production (for each bubble) [#molecules/bubble] is multiplied by the cavitation event rate J [#bubble m^{-3} s^{-1}]. This term is taken in accordance with the work of Delale et al. (2005). The result is a more accurate way to see the radical production because it considers the actual portion of bubble which undergoes cavitation by using the nucleation event rate J.

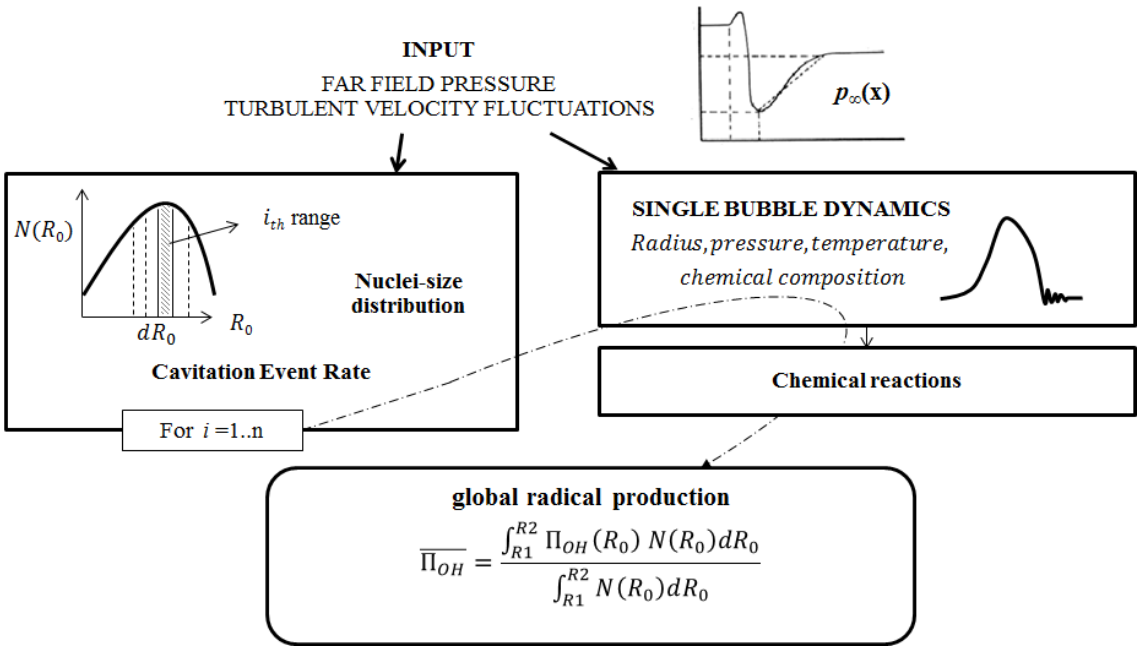

Figure 2: Representation of the mathematical algorithm for simulating the hydroxyl radicals' production

$$\Pi_{OH}(R_0) = J(R_0) \cdot \pi_{OH}(R_0) \tag{1}$$

By introducing a bubble size distribution it is possible to compare different experimental conditions in terms of chemical effect (•OH molecules production). A fixed bubble radius makes the result itself less general and less comparable to empirical observation. For this reason our results will consider an initial bubble distribution as suggested by Liu and Brennen (1998). Thus, the results are averaged over the nuclei distribution in order to obtain a result independent from the initial value R_0 (Capocelli et al., 2013; Colussi et al., 1998) and reported in Eq.(2). Our calculations span the range bracketed by R_0= 20-200 μm:

$$\overline{\Pi_{OH}} = \frac{\int \Pi_{OH}(R_0)\, N(R_0)\, dR_0}{\int N(R_0)\, dR_0} \tag{2}$$

4. Results and Discussion

The simulation of radical production Π_{OH} [mol m^{-3} s^{-1}] is numerically calculated at different inlet pressures P_1 and orifice-to-pipe diameters β = d_p/d_o. The results are shown in Figure 3. It is possible to observe the existence of a higher effective zone, at low β and pressure values in proximity of P_1 = 4 bar. The effect of orifice-to-pipe ratio appears to be monotonically negative: the lower the β, the higher the mechanical energy dissipated and the higher pressure drop occurring into the Venturi. This turns into a higher tension applied to the bubble for growing up and in more frequent cavitation events. These phenomena are accompanied by a higher mass of vapor in the collapsing bubble and more •OH generated. The effect of orifice-to-pipe ratio (in the investigated conditions) is in accordance with literature suggestions (Sharma et al., 2008). The inlet pressure, instead, shows a non-monotonic influence with a peak around 4 bar for every level of β. This is due to the simultaneous presence of different effects which act in opposition: the

higher the pressure is, more rapidly the bubbles collapse because of the turbulence stresses, resulting in a lower specific radical production; on the contrary, by increasing the pressure value (below the limit of supercavitation) the number of actual cavitation nuclei is greater with a positive effect of radical generation. Although this may appear a simplistic view of the involved phenomenology, many literature works recognize the existence of an optimal pressure level, in relation to features acting in contrast (Kumar et al.,2011, 2013; Khrishnan et al.,2006).

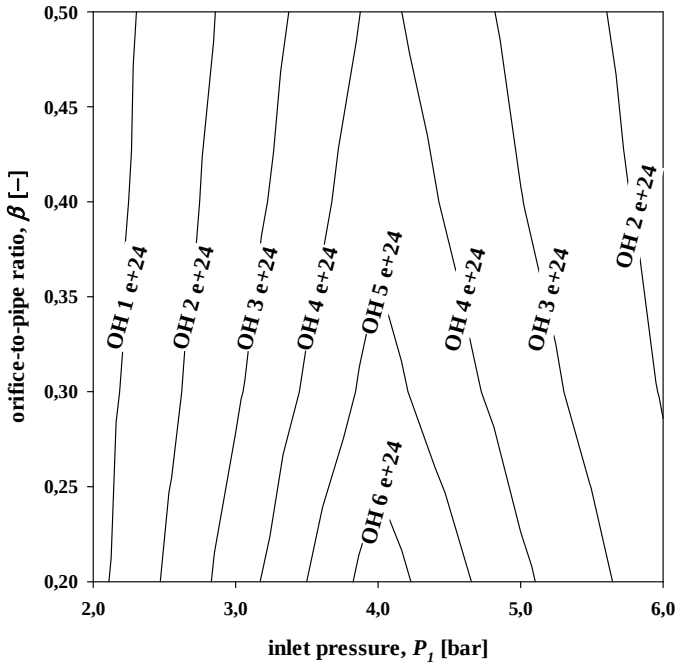

Figure 3: hydroxyl radical production Π_{OH} [#molecules m^{-3} s^{-1}] in relation to the inlet pressure P_1 and the orifice-to-pipe ratio β

The combined effect of β and P_1 has been analyzed by several simulations; the surface which better interpolates numerical results (β, P_1, $\bullet OH$) is a paraboloid; in order to increase the predictive capacity of the Venturi advanced oxidation, a correlation has been proposed in Eq.(3):

$$OH = a_0 + a_1 \cdot P_1 + a_2 \cdot \beta + a_3 \cdot P_1^2 + a_4 \cdot \beta^2 + a_5 \cdot P_1 \beta \tag{3}$$

with the coefficients a_i reported in Table 1. This relationship can be useful in predicting the effectiveness of the Venturi reactor in terms of •OH production. The fifth coefficient a_5 incorporates the effect of correlation between the studied parameters. It is important to mention that the other geometrical characteristics except β, are fixed, the initial bubble size distribution included. A parity diagram is reported in Figure 4 to check for the effectiveness of the proposed relationship in interpolating the results.

Table 1: Parameters a_i to be used in the theoretical correlation of Eq.(3)

a_0	a_1	a_2	a_3	a_4	a_5
-14,1763	11,9243	-13,7244	-1,3901	14,5596	-0,7705

The experimental results of p-nitrophenol dosimetry can be directly compared with the theoretical prediction of the optimal radical production as a function of the inlet pressure. The experimental results are reported in Figure 5, where time profiles of dimensionless concentration are visible (at different pressure levels). The effect of pressure is non-monotonic showing a higher degradation rate around 4 bar. The 4.5-bar curve shows a final degradation percentage at 30 min of 24 %, while at 3.5 and 5 bar it is about 16 %. At values outside the cited range, the chemical effect is negligible: the final removal percentage is comparable with the experimental errors. The existence of an optimal pressure value at a fixed geometry comes from the combination of two aspects: increased number of cavities at higher pressures and higher

specific production π_{OH} at the lower ones. Such observation is extensively confirmed by other experimental works: there is an optimum of the inlet pressure (at a constant flow rate) that should be used for getting the maximum benefits from the system (Kumar et al., 2011, 2013). The range identified in the current paper corresponds to the one suggested by the cited works and finds a good theoretical explanation in the described numerical results which individuated an optimal inlet pressure at 4 bar.

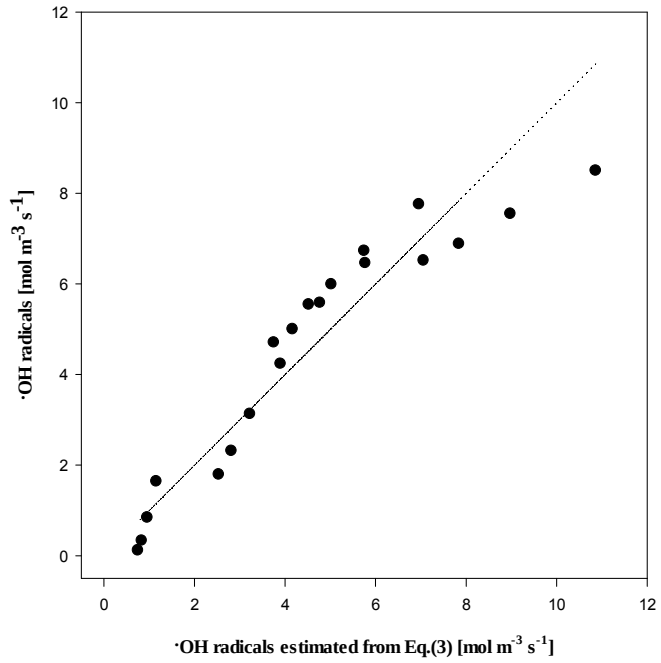

Figure 4: Comparison in terms of hydroxyl radical production between the simulation results and the correlation given in Eq.(3)

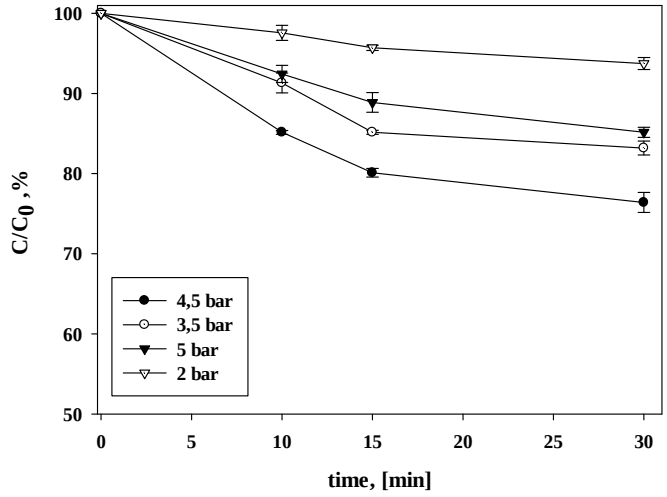

Figure 5: Dimensionless p-nitrophenol concentration versus time, for 4 different levels of inlet pressure for the Venturi device in Figure 1

5. Conclusion

The present work studies the chemical effect of a Venturi reactor. The effect of inlet pressure and orifice-to-pipe ratio has been theoretically described and numerically simulated. From an experimental point of view, the optimal pressure has been found in the range of 3.5-4 bar. Additionally the experimental results confirm the trend showed by the implementation of the mathematical algorithm, which suggests an optimal pressure of *circa* 4 bar for different values of the orifice-to-pipe ratio. The validation of the model can possibly bring a new instrument to design cavitational reactors in the field of environmental applications.
Moreover the numerical simulations should be improved and extended to a larger variation of parameters in order to realize more sophisticated correlations. The addition of bubble population phenomena such as fission and coalescence, with the analysis of transport phenomena (for different chemical species) will be the ultimate step forward in the simulation of environmental application of hydrodynamic cavitation.

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