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Modeling of cavitation as an advanced wastewater treatment

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ABSTRACT

This paper presents a theoretical study of cavitation as an advanced oxidation process. A mathematical algorithm, which couples single bubble dynamics and chemical reactions for a cavitating bubble, is proposed and compared with experimental and theoretical works reported in the literature. The main output variable, used for comparison, is the hydroxyl radical production. A wide range of parameter values is evaluated for the analysis of hydrodynamic cavitation in an orifice. Thanks to the large number of simulation, it was possible to find a very good agreement with a design correlation proposed in the literature. Additionally, a novel approach has been proposed, which consists of integrating the estimated radical production over a typical bubble size distribution in order to predict a global oxidant production. Moreover, by fixing the values of flowrate, pressure, and geometric parameters, a real experimental condition of hydrodynamic cavitation in a Venturi device has been simulated. This allowed the comparison of simulation results with the experimental ones reported in the literature. A good agreement has been found in terms of cavitational yield, an estimation of the process efficiency from an energetic perspective.

Keywords: Advanced oxidation processes; Hydrodynamic cavitation; Theoretical modeling; Hydroxyl radicals

1. Introduction

Increasing requirements of human beings have led to the presence of new toxic, biorefractory, and chemically stable compounds in waste water treatments plants, which are not degraded by conventional treatment methods and end up in the environment. The fulfillment of severe water quality standards is especially claimed for those toxic substances and demands the problem of tertiary treatment to innovative technologies [1–3]. A lot of researches have been addressed to this aim in the last decade pointing out the prominent role of nonconventional oxidation techniques called advanced oxidation processes (AOP), which usually operate near ambient temperature and pressure through the releasing of highly oxidative species: ·OH radicals [4].

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In relationship with water treatment, there are several works in the recent literature that have recognized the cavitation to be a valid technique for the treatment of chemical and biological contaminants [2,3,5–8]. Cavitation is the formation of vapor bubbles in a liquid under variation of pressure: bubbles collapse violently in high-energy phenomena after an initial stage of growth; in water solutions this phenomena produces radical species especially hydroxyl radicals. Although there are many promising applications of environmental sonochemistry, there have been few successful applications on industrial scale due to the inefficient conversion of energy in producing ultrasonic cavitation at scaled up applications. As a matter of fact, industrial applications are limited to use of ultrasounds as pretreatments or auxiliary techniques: at moment high efficiency applications are on lab-scale or in combination with other techniques in hybrid AOPs [8,9].

This consideration brought to the rising of hydrodynamic cavitation technologies, which can represent a more efficient and easily manageable surrogate of sonolysis, showing particular advantages in large-scale operations; additionally, this technology can count on a large background of knowledge in fluid dynamic and shows potentialities in optimization and further development [2,7,9,10]. In order to improve cavitational applications, theoretical research is focused on studying the cavitation phenomenology through the modeling of chemical and physical processes involved in cavitation. The practical goal of this analysis is to explain the effect of parameters on the oxidant production (or even on pollutant degradation) and to give mathematical correlations and useful codes for the reactor design stage. For a true analysis of sonochemical effects, complete models have to consider the complex phenomena associated with cavitation such as water condensation and vaporization, gas diffusion, and chemical kinetics [11]. Modeling results can be compared with the measure of the collapse overpressures, with optical measures of bubbles (or bubble clouds) [11] and with the degradation of model compounds: the so-called "dosimetry method," based on organic traps, can give an indirect estimation of the oxidant production [12,13]. The step for a more accurate simulation of cavitational reactors is to integrate bubble, the transport phenomena of compounds and oxidation mechanisms for an accurate prediction of degradation rates [14,15], as well as to introduce bubble interaction phenomena [16,17]. Although cavitation modeling has improved in the last two decades, there is still the need to establish correlations and to give practical and quantitative information about the design of hydrodynamic cavitation reactors that can definitely turn the applications in a consolidated wastewater treatment.

This paper is part of a research activity concerning theoretical and experimental study of cavitation as an advanced oxidation process. In this article, a mathematical algorithm (solved in Matlab™), which couples the Lagrangian approach of single bubble dynamic model with chemical reactions model, is proposed and evaluated in simulating the efficiency of hydrodynamic cavitation techniques.

2. Simulation model

The physical model considered for simulation consists of a spherical cavitating bubble that is carried through a low pressure region and undergoes a violent collapse after an initial stage of expansion. Fragmentation and coalescence phenomena are neglected and bubble remains spherically symmetric during collapse. Pressure p is considered to be uniform both inside the bubble and in the liquid bulk. Because of the large heat capacity of water, bubble wall temperature is constant and equal to the bulk liquid one that in turn is considered to be constant (293 K) and spatially uniform. The contents of the bubble are water vapor and noncondensable gas with gas diffusion negligible if compared to the water vapor mass transfer. The bubble dynamics equation, in the well-known formulation proposed by Keller and Miksis [18] (Eq. (1)), has been used in this work.

$$\left(1-\frac{\dot{R}}{c}\right)\rho R\ddot{R}+\frac{3}{2}\dot{R}^2\rho\left(1-\frac{\dot{R}}{3c}\right) = \left(1-\frac{\dot{R}}{c}\right)[p_\mathrm{i}-p(t)]+\frac{R}{c}\dot{p}_\mathrm{i}-4\eta\frac{\dot{R}}{R}-\frac{2\sigma}{R} \tag{1}$$

where R is the bubble radius, $\dot{R}$ its time derivative and the bubble internal pressure p_i is evaluated by the van der Waals type equation of state; further definitions are in the Nomenclature section. The model has been written in order to approximate the cavitation in different geometries; to calculate the evolution of the far field pressure $p(t)$, Bernoulli equation is solved with the input of the fluid velocity $U(t)$ (Eq. (2)). In the case of water passing through an orifice, this latter can be fixed by the knowledge of the cavitation number Ca and the orifice to pipe ratio β. Additionally, the contribution of the turbulent velocity is considered following the approximation described by Moholkar and Pandit [19]:

$$U(t) = u(t) + \bar{u}'(t)\sin(2\pi f t) \tag{2}$$

where $u(t)$ is the local mean velocity of the fluid, $\bar{u}'(t)$ is the mean fluctuation velocity in isotropic turbulence, and f is the frequency of the perturbations within the turbulent eddies [19]. The model is completed by simulating the adiabatic collapse of the bubble after the maximum isothermal expansion has been reached; further details of the model are given in the work of Colussi et al. [20]. At this stage, the bubble content is simulated as reactive mixtures of compounds that are not able to diffuse out of the bubble. In the model of the reactive air–vapor bubble, 16 chemical species and 45 chemical reactions have been considered. The total rate of change in species concentration due to the chemical contribution $\dot{N}_i^c$ is formulated in Eq. (3).

$$\dot{N}_i^c = V \cdot \sum_j \alpha_{i,j} \cdot (r_{fj} - r_{bj}) \tag{3}$$

where V is the bubble volume, r_{fj} and r_{bj} are the forward and backward reaction rates for the jth reaction, respectively, and $\alpha_{i,j}$ is the stoichiometric weight for the ith specie in the jth reaction. Finally, in order to predict the bubble temperature, chemical reactions rates are coupled with the energy balance (Eq. (4)):

$$\dot{T}\sum_i \frac{\partial e_{t,i}}{\partial T} = 4\pi R^2 k\left(\frac{T_0 - T}{l}\right) - p_i\dot{V} + V \times \sum_j (r_{fj} - r_{bj})\Delta E_j - \sum_i e_{t,i}\dot{N}_i^c \tag{4}$$

where k is the thermal conductivity of the mixture, l is the thermal boundary layer, $e_{t,i}$ is the thermal energy per molecule, and ΔE_j is the reaction energy of process j. Diffusive flux terms have been neglected for simulating the collapse stage, as previously mentioned. A list of reaction parameters and a detailed description of reaction rates equation is found in the work of Toegel [21].

3. Results and discussion

In order to investigate the effect of geometry and pressure in hydrodynamic cavitation, a first set of parameters has been prepared for simulating hydrodynamic cavitation in an orifice (orifice to pipe ratio $\beta = 0.2$–0.6, initial bubble size $R_0 = 1$–$50\,\mu\text{m}$, and fluid pressure upstream the orifice $P_u = 2$–$7\,\text{bar}$). The Weber number criterion is adopted for the estimation of bubble stability and collapse size [22]. The results allow the comprehension and discussion of parameter effect and the validation with similar works reported in the literature. A global representation of the model simulation is given in Fig. 1 that shows ·OH molecules generated during the collapse phase for different bubble radius R_0 and fluid pressure P_u. The effect of upstream pressure is particularly high, if compared to the effect of the initial radius of bubbles.

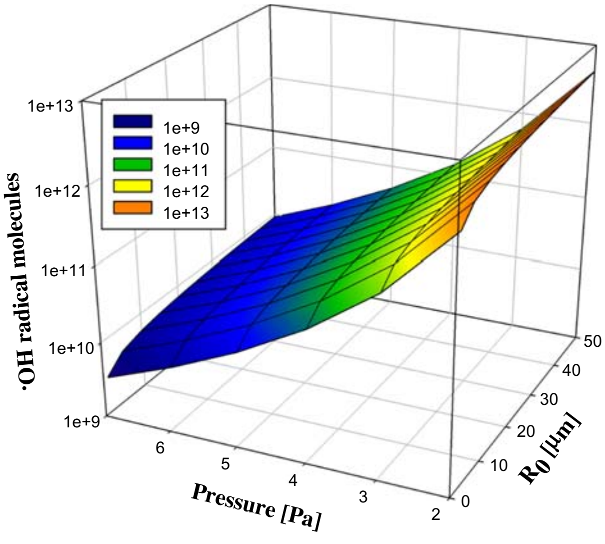

Fig. 1. Simulation results for different bubble radius and fluid initial pressure, Ca = 0.7 and $\beta = 0.5$.

At a fixed cavitation number and an increasing inlet pressure, the fluid throat velocity consequently increases; liquid flow rate and energy dissipation rate across the orifice are higher. This brings to an increase in the fluctuating velocity and a decrease in the maximum possible expansion of the bubble. A less expanding bubble has consequently a minor content of water vapor and a minor capacity in producing hydroxyl radicals. This consideration brings to a reduced oxidant production at higher pressure; this phenomenon is explicitly visible also in Fig. 2(a). This figure shows clearly the described effect of P_u and, additionally, points out the low influence of the bubble initial radius R_0. This behavior is related to the collapse criteria chosen in theoretical modeling: it empathizes the importance of the turbulent stress which is responsible of bubble collapse at similar expansion degrees (the value R/R_0 at the collapse stage is slightly dependent on R_0 [22]). This phenomenon has a direct consequence in similar values of vapor mass fraction inside the collapsing bubbles for different nuclei sizes R_0. Fig. 2(b) shows the effect of the orifice to pipe ratio at a fixed upstream pressure P_u. This effect is mainly due to the reduction of collapse pressure and temperatures in increasing the value of β, as suggested in the literature from theoretical and experimental point of view [7,19,23].

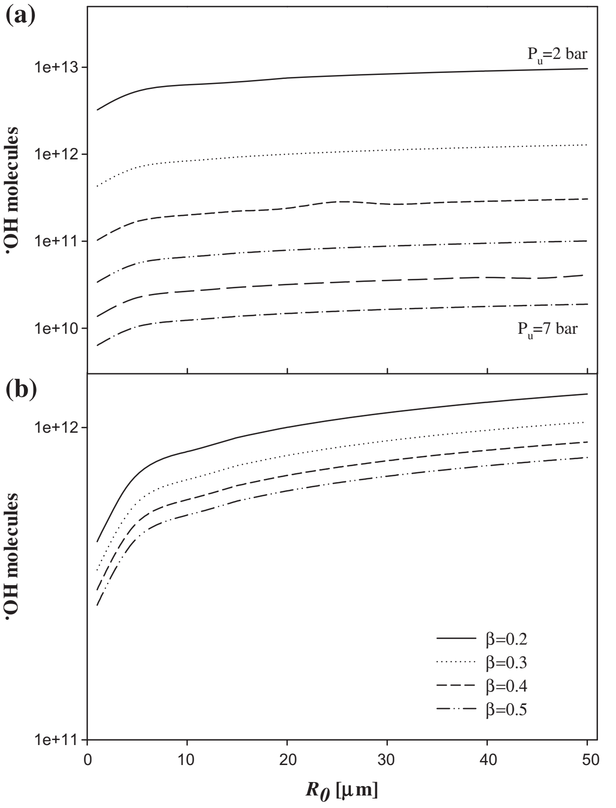

Fig. 2. Simulation of cavitation results through an orifice at Ca = 0.6 for a range of initial nuclei size 1–50 μm. (a) Inlet pressure in the range $P_u = 2$–7 bar with $\beta = 0.2$. (b) Orifice to pipe ratio in the range $\beta = 0.2$–0.5 at $P_u = 3$ bar.

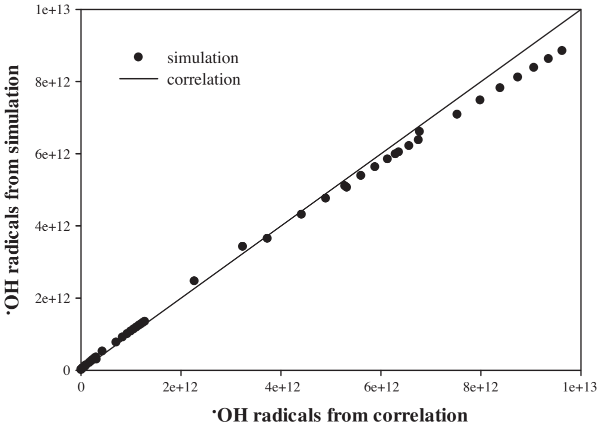

Fig. 3. Comparison between a correlation proposed in literature [22] and our simulation results in predicting the production of hydroxyl radical molecules.

Simulation results can be easily compared with a correlation proposed by Sharma et al. [22]. Fig. 3 shows the comparison in ·OH production between the literature results (x-axis) and our simulation (y-axis) obtained at same conditions; the bisecting line represents a perfect matching between the two results. The very good agreement between our simulation and the literature correlation underlines the goodness of the model and of the approach used in this work.

Typical simulations of hydrodynamic cavitation, such as the ones presented in Figs. 1 and 2, are based upon the assumption of a fixed cavitation number Ca. This assumption establishes a correlation between the fluid pressure and velocity and does not allow a true analysis of a real water treatment, in which the flow rate and the upstream pressure are input parameters, while the cavitation number is a dependent variable. Considering a possible coupling of pressure drop and flow rate (with different cavitation numbers) for a given geometry is a more sophisticated approach that brings to realistic consideration about cavitational reactor efficiency. At this purpose, the theoretical model has been used to simulate the results of an experimental investigation reported in the literature [13], regarding the cavitational efficiency estimated in a Venturi device. The method used for this purpose is that by Morison and Hutchinson [13], which consists of the evaluation of iodide to iodine oxidation during cavitation, a widely used test reaction for the study of the sonochemical effect during cavitation (known as Weissler reaction [24]). To better approximate the reactor geometry, the mean velocity profile can find thanks to the continuity equation, by the knowledge of the reactor section; further details of this approach are described in the work of Kumar and Moholkar [25].

Moreover, since actual experiments reflect a distribution of bubble size, it is useful to integrate our results over an initial bubble size distribution. For this purpose, we assume that homogeneous nucleation takes place in the liquid phase in the presence of stabilized air bubbles which act as cavitation nuclei. The theoretical hydroxyl radical production for each bubble size is integrated over a steady state nuclei size distribution $N(R_0)$ [26]. This calculation allows the estimation of a total radical production Γ_{OH} (Eq. (5)), not strictly dependent on a single R_0 value.

$$\Gamma_{\mathrm{OH}} = \int \delta_{\mathrm{OH}} N(R_0) \mathrm{d}R_0 \tag{5}$$

A useful way to express a global result is by calculating the cavitational yield Y (mol/J), an evaluation of the global energy efficiency of the treatment. For the production of hydroxyl radicals, this parameter can be written as in Eq. (6) and represents the ratio of ·OH moles produced per second on power consumption:

$$Y = \frac{Q \cdot \Gamma_{\mathrm{OH}}}{Q \cdot \Delta P} \tag{6}$$

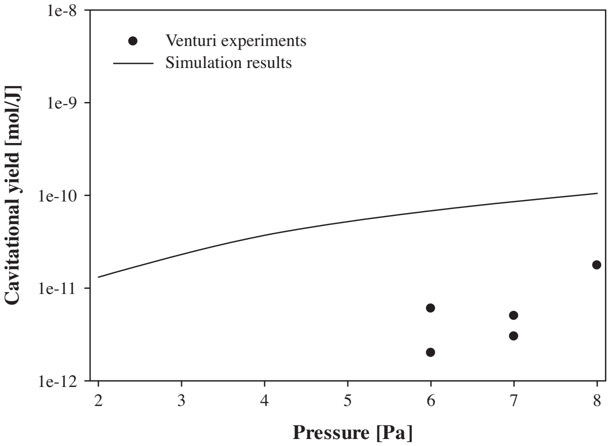

Fig. 4. Cavitational yield Y (straight line) as a function of pressure; line: model results; and full dots: experimental results of Morison and Hutchinson [13].

where Q is the flow rate and ΔP is the system pressure drop. Fig. 4 shows the cavitational yield in hydroxyl radical production Y simulated for the configuration proposed by Morison and Hutchinson [13]. They report a cavitational yield for the I_3^- generated in their experiments (Weissler reaction), indirect estimation of the efficiency in $^{\cdot}$OH production. As also suggested in the literature [17,25,27], higher levels of pressure bring to increasing bubble expansion, more violent collapse and to enhancement in temperature and pressure peaks, moreover the amount of diffusing vapor increases due to a larger expansion of the bubble. Overall, the radical production is higher and the energy efficiency increases although the more energy is needed to produce high level of pressure. The described trend is shown in Fig. 4 and it is in agreement with the observed one. The discrepancy has one main reason: the generation of I_3^- is the result of a complex reaction that can give only the order of magnitude of apparent $^{\cdot}$OH radicals produced. Particularly, the overestimation of simulation results may be attributed to nonconsidered reactions, such as the formation of hydrogen peroxide and its scavenging reactions during iodide oxidation.

4. Conclusions

This paper presents a mathematical algorithm that couples single bubble dynamics and chemical reactions for a cavitating bubble; the model results coming from this approach have been validated by comparing the results with theoretical and experimental works reported in the literature. This kind of modeling is suitable for predicting parameter influence for different geometries and for giving theoretical correlation, useful in the reactor design stage. Additionally, the simulation of a real hydrodynamic system and the integration of results upon an initial nuclei distribution can give a global quantification of the cavitational efficiency. This approach, with further improvements, might be suitable also for predicting directly the degradation of target compounds in a cavitational reactor.

Nomenclature

c	—	velocity of sound in the medium, m/s
Ca	—	cavitation number
e	—	thermal energy of molecules, J/mol
E	—	energy of reaction, J
f	—	frequency of turbulent perturbations, Hz
k	—	thermal conductivity, W/m K
l	—	length of thermal boundary layer, m
N	—	bubble size distribution, m^{-4}
N^c	—	rate of change in concentration (chemical contribution), mol/s
p	—	pressure, Pa
p_i	—	pressure inside the cavitating bubble, Pa
P_u	—	fluid pressure upstream the cavitating device, Pa
Q	—	flow rate, m^3/s
R	—	bubble radius, m
r_b	—	backward reaction rate, mol/m^3 s
r_f	—	forward reaction rate, mol/m^3 s
T	—	temperature, K
U	—	fluid velocity, m/s
u'	—	fluctuation velocity, m/s
V	—	bubble volume, m^3
Y	—	cavitational yield, mol/J

Greek symbols

α	—	stoichiometric coefficient
β	—	orifice to pipe ratio
δ_{OH}	—	specific hydroxyl radical production, mol/bubble
Γ_{OH}	—	total hydroxyl radical production, mol/m^3
η	—	kinematic viscosity, m^2/s
ρ	—	density, kg/m^3
σ	—	surface tension of water, N/m

Superscript

$\cdot$	—	time derivative

Subscript

0	—	initial value

References

[1] T. Mandal, S. Maitya, D. Dasgupta, S. Datta, Advanced oxidation process and biotreatment: Their roles in combined industrial wastewater treatment, Desalination 250 (2010) 87–94.

[2] P.G. Gogate, A.B. Pandit, A review of imperative technologies for wastewater treatment I: Oxidation technologies at ambient conditions, Adv. Environ. Res. 8 (2004) 501–551.

[3] V. Belgiorno, L. Rizzo, D. Fatta, C. Della Rocca, G. Lofrano, A. Nikolau, V. Naddeo, S. Meric, Review on endocrine disrupting-emerging compounds in urban wastewater: Occurrence and removal by photocatalysis and ultrasonic irradiation for wastewater reuse, Desalination 215 (2007) 166–176.

[4] R. Andreozzi, V. Caprio, A. Insola, R. Marotta, Advanced oxidation processes (AOP) for water purification and recovery, Catal. Today 53 (1999) 51–59.

[5] L. Mezulea, S. Tsyfanskyb, V. Yakushevichb, T. Juhna, A simple technique for water disinfection with hydrodynamic cavitation: Effect on survival of Escherichia coli, Desalination 28 (2009) 152–159.

[6] P.G. Gogate, Application of cavitational reactors for water disinfection: Current status and path forward, J. Environ. Manage. 85 (2007) 801–815.

[7] P.R. Gogate, A.B. Pandit, A review and assessment of hydrodynamic cavitation as a technology for the future, Ultrason. Sonochem. 12 (2005) 21–27.

[8] N.N. Mahamuni, Y.G. Adewuvi, Advanced oxidation processes (AOPs) involving ultrasound for waste water treatment: A review with emphasis on cost estimation, Ultrason. Sonochem. 17 (2010) 990–1003.

[9] P.G. Gogate, A.B. Pandit, A review of imperative technologies for wastewater treatment II: Hybrid methods, Adv. Environ. Res. 8 (2004) 553–597.

[10] M. Sivakumar, A.B. Pandit, Water treatment: A novel energy efficient hydrodynamic cavitational technique, Ultrason. Sonochem. 9 (2002) 123–131.

[11] M.P. Brenner, S. Hilgenfeldt, D. Lohse, Single-bubble sonoluminescence, Rev. Mod. Phys. 74 (2002) 425–484.

[12] S.S. Arrojo, C. Nerin, Y. Benito, Application of salicylic acid dosimetry to evaluate hydrodynamic cavitation as an advanced oxidation process, Ultrason. Sonochem. 14 (2007) 343–349.

[13] K.R. Morison, C.A. Hutchinson, Limitations of the Weissler reaction as a model reaction for measuring the efficiency of hydrodynamic cavitation, Ultrason. Sonochem. 16 (2009) 176–183.

[14] T. Sivasankar, V.S. Moholkar, Physical features of sonochemical degradation of nitroaromatic pollutants, Chemosphere 72 (2008) 1795–1806.

[15] T. Sivasanakar, V.S. Moholkar, Physical insights into the sonochemical degradation of recalcitrant organic pollutants with cavitation bubble dynamics, Ultrason. Sonochem. 16 (2009) 769–781.

[16] Y. Iida, M. Ashokkumar, T. Tuziuti, T. Kozuka, K. Yasui, A. Towata, J. Lee, Bubble population phenomena in sonochemical reactor: II. Estimation of bubble size distribution and its number density by simple coalescence model calculation, Ultrason. Sonochem. 17 (2010) 480–486.

[17] X. Zhang, Y. Fu, Z. Li, Z. Zhao, The numerical Simulation of collapse pressure and boundary of the cavity cloud in Venturi, Chinese J. Chem. Eng. 17 (2009) 896–903.

[18] J.B. Keller, M.J. Miksis, Bubble oscillation of large amplitude, J. Acoust. Soc. Am. 68 (1980) 628–633.

[19] V.S. Moholkar, A.B. Pandit, Bubble behavior in hydrodynamic cavitation: Effect of turbulence, AIChE J. 43 (1997) 1641–1648.

[20] A.J. Colussi, L.K. Weavers, M.R. Hoffmann, Chemical bubble dynamics and quantitative sonochemistry, J. Phys. Chem. A 102 (1998) 6927–6934.

[21] R. Toegel, Reaction-diffusion kinetics of a single sonoluminescing bubble, PhD Thesis, University of Twente, 2002.

[22] A. Sharma, P.G. Gogate, A. Mahulkar, A.B. Pandit, Modeling of hydrodynamic cavitation reactors based on orifice plates considering hydrodynamics and chemical reactions occurring in bubble, Chem. Eng. J. 143 (2008) 201–209.

[23] J.S. Krishnan, P. Dwivedi, V.S. Moholkar, Numerical investigation into chemistry induced by hydrodynamic cavitation, Ind. Eng. Chem. Res. 45 (2006) 1493–1504.

[24] A. Weissler, H.W. Cooper, S. Snyder, Chemical effect of ultrasonic waves: Oxidation of potassium iodide solution by carbon tetrachloride, J. Am. Chem. Soc. 72 (1950) 1769–1775.

[25] K.S. Kumar, V.S. Moholkar, Conceptual design of a novel hydrodynamic cavitation reactor, Chem. Eng. Sci. 62 (2007) 2698–2711.

[26] Z. Liu, C.E. Brennen, Cavitation nuclei population and event rates, J. Fluid. Eng. T. ASME 120 (1998) 728–737.

[27] A.A. Pradhan, P.R. Gogate, Removal of p-nitrophenol using hydrodynamic cavitation and Fenton chemistry at pilot scale operation, Chem. Eng. J. 156 (2010) 156.