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Sarvothaman, V. P., Nagarajan, S., & Ranade, V. V. (2018). Treatment of Solvent Contaminated Water using Vortex based Cavitation: Influence of operating pressure drop, temperature, aeration and reactor scale. *Industrial and Engineering Chemistry Research*. <https://doi.org/10.1021/acs.iecr.8b01688>

Published in:
Industrial and Engineering Chemistry Research

Document Version:
Peer reviewed version

Queen's University Belfast - Research Portal:
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Treatment of Solvent Contaminated Water using Vortex based Cavitation: Influence of operating pressure drop, temperature, aeration and reactor scale

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Abstract

Hydrodynamic cavitation is being increasingly pursued for developing intensified and compact wastewater treatment process. Experimental data on the degradation of water contaminated with three commonly used solvents – acetone, ethyl acetate (EA) and isopropyl alcohol (IPA) using vortex based cavitation devices is presented. Influence of operating flow or pressure drop across cavitation device (150 to 300 kPa), operating temperature (20 to 45 °C), concentration of pollutant (1000 ppm to 50000 ppm) and scale of cavitation reactor (with scale – up factor of 4 maintaining the geometric similarity) has been reported. A new reaction engineering model based on the number of passes through cavitation device was developed to interpret degradation behaviour. The model provides a convenient way to estimate the per-pass degradation factor from batch experiments, allows its extension to continuous processes and to more sophisticated models of estimating generation of hydroxyl radicals. The model showed excellent agreement with experimental data. The per-pass degradation factor exhibited a maxima with respect to pressure drop (200 – 250 kPa) across cavitation device. Aeration was found to improve degradation performance up to 1 vvm ($[L/min]_{gas}/[L/liquid]$). The initial concentration of acetone (1000 to 50000 ppm) and IPA (1000 to 22000 ppm) was found to have negligible effect on degradation performance. The per-pass degradation factor for EA was 1.5 and 4 times of Acetone and IPA respectively. The effect of two scales (nominal capacities of the small and large-scale devices used were 0.3 m³/hr and 1.2 m³/hr respectively) was investigated for the first time and it was found that per-pass degradation factor decreased with scale. The presented model and experimental data provide new insights into application of hydrodynamic cavitation for wastewater treatment and provide a basis for further work on scale-up of hydrodynamic cavitation devices. The results will be useful to researchers as well as practicing engineers interested in harnessing hydrodynamic cavitation for water treatment.

Key words: hydrodynamic cavitation, vortex, per-pass degradation, aeration, scale-up

1. Introduction

Water used in industries for variety of purposes ends up as waste water contaminated by organics, and thus requires treatment before discharge or reuse. There is an increasing interest in using advanced oxidation processes (AOP) for effective wastewater treatment (WWT). A number of AOP's and their combinations have been reported in literature for WWT, which include - Fenton's/photo-Fenton's reactions, ozonation, photocatalysis, UV/H₂O₂ treatment, ferrate treatment, electrochemical treatment and cavitation (1-5). Cavitation realises in-situ generation of hydroxyl radicals without requiring any external oxidants or chemicals and therefore offers an attractive process for WWT (6).

Cavitation is the phenomenon of formation, growth and collapse of cavities (microbubbles). Collapsing cavities generate very high localised temperature and pressure which in turn generates strongly oxidative hydroxyl radicals (7). Cavitation can be realised either ultrasonically or hydro-dynamically (7-9). Ultrasonic cavitation is energy intensive and is difficult to scale up (10). Hydrodynamic cavitation devices, on the other hand can be scaled up relatively easily and are energy efficient (6, 11). Therefore, there is an increasing interest in using hydrodynamic cavitation for treatment of a range of effluents and industrial wastewaters (1, 2, 12 - 16). Orifice, venturi or rotor-stator assemblies are some of the commonly studied hydrodynamic cavitation devices (10 - 12, 17). In these devices, cavitation occurs along the walls which eventually leads to erosion and therefore deterioration of performance of the device. These devices use either small constrictions or expensive rotating equipment which are usually not suitable for WWT. Recently, Ranade *et al.* (18, 19) have disclosed a novel vortex based cavitation device for effluent treatment. This device uses swirling flow in a novel configuration to generate cavitation. This vortex based cavitation device has shown to perform better than orifice based cavitation device for variety of applications (1, 20, 21). The device offered 3 to 8 times better cavitation yield (mg pollutant degraded/Joules) compared to the orifice plate. These early studies were focussed on demonstrating the advantages and overall performance of the developed vortex based cavitation device. Though some results on influence of flow rate or pressure drop on degradation performance are available, no systematic information on influence of other important parameters like operating temperature, concentration of pollutant, aeration and most importantly of scale of operation is available. The systematic information about these parameters is not available even for the other commonly used cavitation devices like orifice or venturi. In this work, we report experimental data on treatment of water contaminated with three commonly used solvents namely acetone, ethyl acetate (EA) and isopropyl alcohol (IPA) using vortex based cavitation devices. We report influence of flow rate or pressure drop across cavitation unit, operating temperature, concentration of pollutant and scale of cavitation reactor.

Increased operating temperature during cavitation has been reported to improve degradation performance. Higher temperature increases vapour pressure and therefore enhances extent of cavitation (generated number density of cavities, n_c , number/m³s). Patil and Gogate (22) studied degradation of methyl parathion using an orifice plate as the cavitation device (in a narrow range of 305 to 312 K). They reported higher degradation rate at higher temperature. Wang and Zhang (23) performed alachlor degradation experiments in a swirling jet hydrodynamic cavitation reactor and determined the effect of operating temperature (in a range of 303 to 333 K) on the degradation rate. They found that degradation rate initially increased with temperature up to 313 K, beyond which it was found to plateau or decrease. Similar observation with increase in temperature was made by Braeutigam *et al.* (24) for the degradation of carbamazepine by hydrodynamic-acoustic-cavitation. In this work we have analysed influence of temperature on degradation performance up to temperature of 318 K. We report degradation data obtained under non-isothermal conditions and use this data for developing an appropriate non-isothermal modelling framework for cavitation. Aeration of wastewater is known to enhance the concentration of dissolved air and will provide more nuclei for cavitation. Gogate (25) has reviewed studies reporting influence of aeration on performance of acoustic cavitation. However, studies on influence of aeration on performance of hydrodynamic cavitation are scarce (1, 17). Suryawanshi *et al.* (1) performed solvent degradation experiments and reported about 10 % increase in degradation performance in presence of aeration compared to that without aeration. This marginal increase was attributed to the availability of additional oxygen for the oxidation process and enhanced inception of cavitation due to gas/vapour nuclei formed as a result of aeration. In this work we report influence of aeration on degradation of acetone.

None of the previously published studies report influence of scale of cavitation device on WWT. Most of the published studies use ad-hoc designs of cavitation devices. Saharan *et al.* (25) performed orange-G degradation experiments using two types of venturi tubes (circular and slit venturi) and an orifice plate as the different hydrodynamic cavitation devices. They reported that the slit venturi performed better in terms of decolourisation when compared to the other two devices for similar initial conditions. Sivakumar and Pandit (26) performed experiments on the degradation of rhodamine B dye using a number of multiple-hole orifice plates and reported that the orifice plate with the higher number and smaller diameter of holes performed better. However, because of non-uniform designs used in published studies, it is almost impossible to understand influence of scale of cavitation device on degradation performance from the available results. In this work, we use commercially available, standard vortex based cavitation devices and report for the first time, the influence of scale on degradation performance using two geometrically similar cavitation devices (scale – up factor of 4).

Most of the previously published studies on pollutant degradation using hydrodynamic cavitation have reported the use of an effective rate constant estimated from batch experiments to characterize the effect of operating conditions (like pressure drop across cavitation device) and nature of pollutants (see for example, 15, 16, 25 and references cited therein). This approach has been used in numerous reports using different cavitation devices. Unfortunately, this approach is not very useful to connect the effectiveness of degradation to the flow characteristics of cavitation device. The approach therefore is not useful to design industrially relevant large scale and continuous wastewater treatment based on hydrodynamic cavitation. A typical cavitation based water treatment set-up is shown in Figure 1. For most of the cases, multiple passes through cavitation device are needed to achieve desired reduction in pollutant concentration. For a continuous system, this translates into the decision of selecting appropriate flow rate through cavitation device (Q) for a given net flow rate of waste water stream (q) for a desired reduction in the pollutant concentration (C_{in} to C). It is therefore essential to develop a framework for modelling pollutant degradation using hydrodynamic cavitation based on effective per-pass degradation occurring in the cavitation device. The per-pass degradation can then be related to flow characteristics and operating parameters of the cavitation device and appropriate scale-up models can then be developed. In this work, we have developed such a framework for describing wastewater treatment using hydrodynamic cavitation.

Figure 1: Representation of a typical cavitation set-up used in industry

We report here a systematic framework to determine per-pass degradation factor from the batch experiments. The model is extended to account for non-isothermal effects commonly encountered in batch experiments with hydrodynamic cavitation. The scope here is limited to lumped reaction engineering like models. The framework however provides a convenient way to connect with more sophisticated models of cavity dynamics and computational fluid dynamics to evolve a comprehensive multi-scale design platform for hydrodynamic cavitation. The data of treatment of water contaminated with three commonly used solvents at different operating conditions (pressure drop, temperature, initial concentration and aeration) and at two different scales along with the systematic modelling framework based on per-pass degradation factor presented here will be useful for design and application of hydrodynamic cavitation based water treatment solutions.

2. Experimental

The experimental setup designed for this work was similar to hydrodynamic cavitation reactor setups used in literature (1, 12, 15, 17, 22, 26 – 28). The experimental set-up was designed to ensure that under the desired operating conditions, cavitation occurred only in the device but not the pump or the valves. The experimental setup (Figure 2a) consisted of a holding tank (total volume of 0.093 m³) from which the liquid was pumped using a Grundfos CM 1-5 self-priming pump (2900 rpm, 50 Hz, single phase). The pump discharge pressure was set to 300 kPa or 350 kPa to ensure that there was no pump cavitation. This discharge line branched into a bypass line and the main feed line and both these lines were directed back to the holding tank with necessary fittings. Multiple valves were placed in the flow line to ensure that there is no cavitation across valves. A stethoscope was used to identify cavitation noise. Manual measurements using the stethoscope were used to ensure that there is no other cavitation occurring in the flow circuit except that occurring in a cavitation device. Pre-calibrated analogue pressure gauges procured from Thermosense Direct (P1 – downstream of the pump and P2 – upstream of the diode) in the ranges of 0 – 700 kPa and 0 – 400 kPa respectively were used to monitor the pressure. A pre-calibrated Gardena smart meter (Art 8188) was used downstream of the cavitating device to monitor the liquid flow rate. The vortex based cavitation devices manufactured in stainless steel were procured from Vivira Process Technologies (www.vivira.in).

Two similar experimental set-ups were constructed with two geometrically similar vortex based cavitation devices. The geometrical details of vortex based cavitation devices can be found in Ranade *et al.* (18). The pictorial version of cavity generation in these types of cavitation devices is shown in Figure 2b. The key characteristics of the two set-ups are listed in Table 1.

(a) Schematic of experimental set-up

(b) Pictorial representation of vortex based cavitation devices

Figure 2: Experimental set – up and vortex based cavitation device

Table 1: Details of two experimental set-ups

Cavitation device	Throat diameter, mm	Nominal capacity, m ³ /hr	Working liquid volume, m ³ (unless mentioned otherwise)
Small (S)	6	0.3	0.0093
Large (L)	12	1.2	0.015

In typical experiments, solvent contaminated water was circulated through the cavitation set-up shown in Figure 2a. Three solvents: acetone (HPLC grade purchased from Sigma-Aldrich), EA (HPLC grade purchased from VWR, UK) and IPA (ACS reagent purchased from VWR, UK) were used. The set-up was initially filled with distilled water. Desired quantity of solvent (as per desired initial concentration) was then added to the holding tank while distilled water was being recirculated. The contents were circulated for 10 minutes (more than 3 residence times) to achieve complete mixing. The initial temperature was recorded using a digital thermometer, and sample at time 0 minutes was taken. Samples were then taken at regular intervals of 30 minutes for 4 hours with the corresponding measurement of the bulk temperatures. These typical experiments were performed in triplicates to determine the error bars between different sets. For carrying out experiments at different temperature conditions, indirect cooling with an ice filled beaker placed in the holding tank was used. For experiments with aeration, a measured flow of compressed air was sparged into the holding tank via home-made sparger. Unless mentioned otherwise, results are of the small cavitation device, S.

UV spectrometry was used to measure the absorbance of the acetone samples to indirectly monitor its concentration. 10000 ppm stock solution of acetone was prepared. From this stock solution, a range of concentrations from 0 – 1000 ppm (with 200 ppm increments), in triplicates were prepared

by diluting with the required amount of distilled water. A volume of 1.5 ml from each concentration was taken in a quartz cuvette and the absorbance was measured using a Cary 300 Scan, UV-Visible Spectrophotometer at a wavelength of 263 nm. Distilled water was used as the blank for absorbance measurements. The absorbance spectra obtained for the samples were subtracted with the blank's absorbance spectra to determine the actual absorbance for each concentration. A standard curve was then plotted as absorbance at 263 nm against acetone concentration. The measurements were recorded in triplicates and the error bars were determined (errors were less than 1%). The equation obtained from the standard curve was used to determine the concentration of the unknown sample obtained from the cavitation experiments.

The concentrations of IPA and EA were indirectly quantified by measuring chemical oxygen demand (COD). The relative time required for the analysis and availability of analytical equipment played a role in using different techniques for different pollutants. In this case, since separation and by-product identification were not the primary goals, simple concentration determination techniques such as spectrometry and COD analysis were opted. Since spectrometry was a quick and reliable method, with acetone showing a maximum absorbance at 263 nm, it was used to monitor the concentration of acetone. In the case of IPA or EA, since a wavelength with clear maximum absorbance was not observed using spectrometry, an indirect method such as COD analysis was used. We have however ensured that the ratio of concentration to initial concentration is almost the same by using any of the techniques. This was established by comparing measurements of acetone by UV and COD. COD was measured using a Spectroquant Move 100 (Merck) spectrophotometer after digesting 2mL samples with the commercially available COD reagent kits (TNT, 0 - 1500 mg/L O₂, purchased either from Hach UK or Merck UK) for 2 hours at 150 °C.

3. Mathematical Model

In a hydrodynamic cavitation device, cavities are generated as a result of low pressure regions formed in the flow path. These cavities oscillate because of turbulent pressure fluctuations and subsequently collapse upon a rapid increase in bulk pressure. The implosion of these bubbles lead to high localised pressure and temperatures. These extreme conditions give rise to the generation of reactive radical species from water (7). These radicals ($R^\cdot$) are quite reactive and rapidly react with pollutant as well as other species in wastewater (including water itself). A recent review states (29) that reaction rate constants of OH radicals with a range of pollutants to be in the range of $10^8 - 10^{10} \text{ M}^{-1} \text{ s}^{-1}$. There are several attempts to understand radical formation and their subsequent reactions with pollutants (see for example reaction schemes proposed by Saharan et al. (7) and references cited therein). However,

because of extreme reactivity of the generated radicals, it is extremely difficult to quantify their concentration or different reaction pathways. It is therefore customary to approximate pollutant degradation in a simplistic manner such as:

Where z_R is a stoichiometric coefficient.

Complete mineralisation of pollutant proceeds via a multi-step unstable organic radical formation. As mentioned earlier, most of the previously published studies on pollutant degradation using hydrodynamic cavitation have reported the use of an effective rate constant estimated from batch experiments. Unlike this, we here develop a framework based on extent of degradation occurring in a single pass through a cavitation device (using per-pass degradation factor). The overall behaviour of a typical cavitation based water treatment set-up shown in Figure 1 can be modelled as:

$$V \frac{dC}{dt} = q(C_{in} - C) - Q\phi C \quad (1)$$

C is a concentration of pollutants, V is a working volume (volume of holding tank and volume of piping including the pump), Q is a flow rate through cavitation device and ϕ is a per-pass degradation factor. If the value of ϕ is assumed to be constant over a range of concentration and time, it can be obtained by running the cavitation set-up in a batch model and using experimental measurement of concentration of pollutant as a function of time and the Equation (1) with $q=0$ as:

$$C = C_{in} e^{-\beta\phi t} \quad (2)$$

Where β is a ratio of flow rate through cavitation device and working volume (Q/V , s^{-1}). The product of β and time indicates number of passes, n , through the cavitation device for a batch system:

$$n = \beta t \quad (3)$$

For a continuous mode of operation, at a steady state, we get:

$$C = \frac{q}{q+Q\phi} C_{in} = \frac{C_{in}}{1+\beta\tau\phi} \quad (4)$$

Where τ is a residence time of the holding tank based on net flow (V/q).

Flow rate through cavitation device can be estimated from desired degradation and system specific value of per pass degradation (for a given device – operating conditions) as:

$$\beta\tau = \frac{Q}{q} = \frac{1}{\phi} \left(\frac{C_{in}}{C} - 1 \right) \quad (5)$$

For example, C_{in} is 1500 ppm and desired outlet concentration at steady state is 500 ppm, flow rate through cavitation device should be $(2/\phi)$ times net flow rate. The cavitation yield, Y (micrograms/J) can be expressed as:

$$Y = \frac{10^{-3}(C_{in}-C)M_{wp}\rho}{\Delta P\beta\tau} = 10^{-3} \left(\frac{\phi C}{\Delta P} \right) M_{wp}\rho \quad \text{kg of COD/kJ} \quad (6)$$

Where ρ is density of liquid and M_{wp} is molecular weight of pollutant.

Per-pass degradation coefficient, ϕ , can be related to generation of hydroxyl radicals in the cavitation device (G , kmol/s) and their subsequent reactions with the pollutant. Considering that radicals have very small life time, τ_R , compared to the residence time in the cavitation device (and downstream piping up to the holding tank), it may be safely assumed that all radicals are consumed within the reactor. Radicals are highly reactive and therefore in addition to reaction R2, radicals may react with any other scavengers present in the liquid (including water itself). Therefore, only a fraction of generated radicals (say, δ) will be used for degrading the pollutant. This fraction may be written as:

$$\delta = \frac{k_2 C}{(k_2 C + k_S C_S)} \quad (7)$$

The per-pass degradation factor can then be related to the generation rate as:

$$Q C \phi = \frac{G \delta}{z_R} \quad (8)$$

The per-pass degradation coefficient can then be written as:

$$\phi = \frac{\left(\frac{G}{Q C_S z_R} \right)}{\left(\frac{k_S + C}{k_2 C} \right)} \quad (9)$$

The per-pass degradation factor will depend on rate of generation of hydroxyl radicals (G), flow rate through cavitation device (Q), chemical nature of pollutant (reactivity with hydroxyl radicals, k_2 and stoichiometric coefficient, z_R and hydrophobicity of pollutant molecules), concentration of the pollutant (C), concentration of scavengers (C_S) and relative rate reactivity of pollutant and scavengers (k_S) with hydroxyl radicals. It can be seen that for low concentrations of pollutant ($C \ll C_S$), the value of per-pass degradation factor will be independent of pollutant concentration. It will essentially

depend on the effective generation rate of hydroxyl radicals, G and the ratio of k_5 to k_2 . As the reactivity of pollutant decreases with respect to reactivity of other existing scavengers, the per-pass degradation factor decreases. G depends on flow characteristics of the cavitation device which controls number density of cavitation events and intensity of cavity collapse (which controls generation of hydroxyl radicals per collapsing cavity). At higher concentrations of pollutant, the Equation (9) indicates that the per-pass degradation factor may slightly decrease with increase in concentration. This is based on the assumption that increase in pollutant concentration is not changing the rate of generation of hydroxyl radicals. However, this may not be realistic in all cases. For pollutants which exhibit more volatility than water, increased concentration of pollutant will lead to significant amount of pollutant in the generated cavity since vapour pressure of the pollutant will not be negligible compared to the water vapour pressure. For example, in a case of 1% (by weight) solution of acetone, the equilibrium vapour will contain ~3% acetone (assuming Raoult's law). The presence of pollutants in vapour cavities will influence generation of hydroxyl radicals as well as will also result in vapour phase thermal degradation of pollutants. In such cases, more sophisticated models will be necessary.

For most of the waste water treatment applications, the presented model will be useful. The value of per-pass degradation factor, ϕ may be obtained by fitting the experimental data using Equation (2). The model presented so far describes the process under isothermal conditions. For non-isothermal operation, the model can be readily extended by relating per pass degradation factor to activation energy as:

$$\phi = \phi_0 e^{-\Delta E/RT} \quad (10)$$

The Equation (2) will then have to be re-written as:

$$C = C_{in} e^{-\beta \phi_0 \int e^{-\Delta E/RT} dt} = C_{in} e^{-\phi_0 \int e^{-\Delta E/RT} dn} \quad (11)$$

The change in temperature may be obtained by writing an energy balance across the reactor if all the thermal losses are known. In commonly used experimental set-ups, the energy used by the pump is dissipated in the form of heat in the circulating liquid and therefore temperature of the liquid rises with time. Heat exchange may be used to control the temperature of the system. Depending on the scale of the experimental system (heat transfer area per unit volume of the system), heat transfer because of natural circulation around the set-up may also lead to nearly constant temperature after rising to a certain level. Experimental data (of concentration and temperature) at different constant temperatures or non-isothermal conditions may be used to obtain values of ϕ_0 and $\Delta E/R$. If non-

isothermal experiment is carried out, a piece-wise linear approximation may be assumed for the measured temperature profile. With this approximation, it is possible to integrate Equation (11) analytically. However the solution involves exponential integration, Ei. In this work, we have used numerical methods using MATLAB instead of using analytical approach. Using the measured values of concentration and temperature, two parameter optimisation may be used to estimate values of $\Delta E/R$ and ϕ_0 . Alternatively, concentration profiles measured at constant temperature may be used to estimate value of $\Delta E/R$ and the data sets may be used to estimate value of ϕ_0 by error minimisation. In this work, we have used the latter approach. We have systematically carried out experiments to evaluate the presented model. The key results are discussed in the following section.

4. Results and Discussion

Systematic experiments to understand the influence of temperature, operating flow or pressure drop across cavitation device, liquid volume, concentration of pollutant, extent of aeration and scale of cavitation reactor on degradation performance were performed. Most of the experiments were performed with acetone as a pollutant. Typical starting concentration of the experiments was in the range of 800 to 900 ppm. After quantifying influence of various parameters on degradation of acetone, additional experiments were carried out to understand influence of nature of pollutant on degradation performance by carrying out experiments with ethyl acetate (EA) and isopropyl alcohol (IPA) as pollutants.

The typical profiles of concentration and temperature for experiments with acetone contaminated water are shown in Figure 3. It can be seen that concentration of acetone is reduced to half in about 100 passes through the cavitation device. Temperature rises by about 20 K during this period. No attempt was made to control the temperature. The system however appears to attain a kind of thermal steady state after nearly 80 passes. The temperature rise for the final two hours of the experiment (for number of passes greater than 80) was quite small (~ 2 K) and can be approximated as a nearly constant temperature data.

The reproducibility of experiments at the operating condition ΔP of 250 kPa was found to be within 5% of three experiments, an error similar to that exists for all other operating conditions. For the sake of clarity, error bars are not always shown in the figures presented here. After establishing reproducibility and required sampling intervals, influence of various operating parameters were investigated. Key results are discussed in the following sub-sections.

Figure 3: Typical concentration and temperature profiles

Pollutant: acetone, Starting concentration, C_0 : 863 ppm, Total liquid volume: 0.0093 m^3 ;
 Pressure drop across cavitation device, ΔP : 250 kPa, Flow rate, Q : $8.08 \times 10^{-5} \text{ m}^3/\text{s}$.
 Solid line indicates predicted concentration profiles ($\Delta E/R=3950$, $\phi_0=1952$); Dotted line indicates piece-wise linear profile of temperature assumed for estimating concentrations.

4.1 Influence of temperature

As seen from temperature profile shown in Figure 3, all non-isothermal experiments exhibited more or less constant temperature region beyond 80 passes through cavitation device. The temperature variation in that region was typically within $\pm 1^\circ\text{C}$. The concentration versus number of passes data obtained over this nearly constant temperature region was processed using Equations (2) and (3) to estimate the per-pass degradation factor (ϕ). Different non-isothermal experiments were carried out by changing initial temperature of effluent water and by placing a beaker filled with ice as the coolant in the holding tank. Experiments exhibiting constant temperature regions over 297 to 317 K were used to estimate influence of operating temperature on per-pass degradation factor at two different operating pressure drops across cavitation device. Equation (10) was used to estimate effective activation energy. The per-pass degradation factors obtained from these experiments are shown in Figure 4.

It can be seen that increase in temperature by 20 K increases per-pass degradation factor by 100%. As discussed in Section 1, increase in temperature may not always result in increased degradation rates/performance. Increase in temperature beyond a certain critical value may lead to excessive

vaporisation which may lead to increased compressibility of the vapour – liquid mixture and reduce intensity of cavity collapse. In some cases, excessive vaporisation may lead to choking cavitation. Degradation rate and therefore effective per-pass degradation factor may therefore reduce with increase in temperature beyond a critical value. However, the experimental data collected in this work (maximum temperature was below 320 K) exhibited monotonic increase in per-pass degradation factor with increase in operating temperature. This is in agreement with earlier studies (22-24). A possibility of acetone loss because of evaporation was evaluated. Though acetone is low boiling (vapour pressure at 313 K is 56245 Pa), the acetone mole fraction is quite small (1000 ppm, mole fraction ~ 0.0003). Therefore even at 313 K, the effective partial pressure of acetone is less than 20 Pa which is quite small to ensure that acetone escaping due to evaporation is negligible.

Figure 4: Influence of temperature on per-pass degradation factor, ϕ .

Pollutant: acetone, Total liquid volume: 0.0093 m³.

Symbols: experimental data; solid and dotted lines: ϕ calculated using Equation (11) with $\Delta E/R = 3950$ K, $\phi_0 = 2550$ for 150 kPa and $\phi_0 = 1950$ for 250 kPa.

The data of concentration versus number of passes may be processed using Equation (11) and two parameter optimisation for obtaining values of ϕ_0 and $\Delta E/R$. The number of experimental data points were however not adequate to carry out systematic two parameter optimisation. In this work, therefore, we approximated activation energy using the limited data points which we had and used one parameter optimisation to calculate per – pass degradation coefficient, ϕ_0 . It can be seen from Figure 4 that the data can be reasonably described by Equation (10) with $\Delta E/R = 3950$ K. The data fit for 250 kPa is not as good as that of 150 kPa. However, since the objective of this work was to present

a new way of modelling hydrodynamic cavitation and the presented one parameter optimisation is reasonably successful in describing the experimental data, we did not make further efforts to improve the fit because of the limited experimental data sets available with us. The approach however can be extended in a straight forward manner for the two parameter optimisation provided adequate number of experimental data points are available.

Therefore, the value of $\Delta E/R$ was set to 3950 K for all subsequent analysis. The value of ϕ_0 appearing in Equation (10) can then be obtained by fitting the non-isothermal model (Equation 11) by minimising errors in fitted and experimental values of pollutant concentration. Experimental temperature profiles were approximated by a piece-wise linear profile for this purpose. The non-isothermal model showed excellent fit with the experimental data (see comparison of predicted and experimental data shown in Figure 3). The values of ϕ_0 obtained by this method for a range of operating conditions, pollutants and scale of cavitation reactors are listed in Table 2.

Table 2: Estimated values of ϕ_0 with $\Delta E/R = 3950$ K

Device	Pollutant	$V \times 10^3$, (m ³)	ΔP , (kPa)	$Q \times 10^4$, (m ³ /s)	C_0 , (ppm)	Aeration (vvm)	ϕ_0 , (-)
S	Acetone	9.3	200	0.73	870	0	1770
S	Acetone	13.9	250	0.81	841	0	1975
S	Acetone	9.3	250	0.81	852	0	1952
S	Acetone	9.3	300	0.88	880	0	1900
S	Acetone	9.3	350	0.95	862	0	1425
S	Acetone	9.3	250	0.81	1000	0.3	2160
S	Acetone	9.3	250	0.81	893	1.01	5000
S	Acetone	9.3	250	0.81	950	1.46	4200
S	Acetone	9.3	250	0.81	8838	0	1950
S	Acetone	9.3	250	0.81	22315	0	2350
S	IPA	9.3	250	0.81	1105	0	820
S	IPA	9.3	250	0.81	10000	0	650
S	IPA	9.3	250	0.81	50000	0	700
S	EA	9.3	250	0.81	725	0	3285
L	Acetone	15	200	3.00	924	0	385
L	Acetone	15	250	3.31	941	0	355
L	Acetone	15	350	3.92	975	0	292
L	Acetone	15	450	4.38	930	0	265

4.2 Influence of liquid volume

In order to demonstrate that the degradation of pollutant is a function of number of passes through the cavitation device and not a function of time, experiments were carried out with two different liquid volumes in the holding tank (0.0093 m³ and 0.0139 m³). The experimentally measured

concentration profiles are shown in Figure 5 as a function of number of passes. It can be seen that though the reduction of concentration with respect to time was much slower for the case with larger liquid volume, the concentration profiles as a function of number of passes do not show any influence of liquid volume. The values of ϕ_0 obtained for these different liquid volumes are within error bars (1952 and 1975: see Table 2). This confirms that overall degradation behaviour of waste water treatment using hydrodynamic cavitation can be appropriately modelled using the per-pass degradation factor.

The per-pass degradation model was then used to interpret the experimental data obtained at different pressure drop across cavitation device.

Figure 5: Influence of vessel volume on degradation performance
Pollutant: acetone, Starting concentration, C_0 : 840 ppm
Pressure drop across cavitation device, ΔP : 250 kPa, Flow rate, Q : $8.08 \times 10^{-5} \text{ m}^3/\text{s}$

4.3 Influence of flow rate through/ pressure drop across cavitation device

It can be seen from Equation (6) that the cavitation yield is proportional to the ratio of per-pass degradation factor and pressure drop across the cavitation reactor for a specific pollutant concentration. It is therefore interesting to see how per pass degradation factor varies with pressure drop.

At very low pressure drop across the cavitation device, flow is not adequate to generate cavitation. For conventional cavitation devices like orifice or venturi, cavitation number is used to estimate inception of cavitation. The cavitation number, Ca is defined as $(\frac{p_2 - p_v}{\frac{1}{2}\rho U_t^2})$, where p_2 is downstream pressure, p_v is vapour pressure and U_t is superficial liquid velocity at the throat (of orifice or venturi). Cavitation inception may occur when Ca falls below unity. However, in reality, the cavitation inception may occur at larger values of Ca when liquid contains some dissolved gases (28). Typical pressure drop required to initiate cavitation is in the range of 300-800 kPa for orifice (26, 30, 31) and 200-500 kPa for venturi (17, 32, 33). Unlike these conventional devices, the vortex based cavitation device used in the present work relies on rotational flows to generate low pressure and therefore cavitation. It has been reported that devices based on rotational flows demonstrate early inception of cavitation (34). In this work, we used stethoscope to manually identify cavitation noise and inception by slowly increasing flow through cavitation device. The data of pressure drop across the cavitation device and flow through the device was collected for the small ("S") and large ("L") cavitation devices (see Figure 6) while stethoscope was used to monitor cavitation noise at different locations in the flow circuit. It can be seen that the pressure drop data can be described by setting Euler number (ratio of pressure drop and velocity head at the throat of the cavitation device) as 60.

Figure 6: Pressure drop and flow rate relationships for vortex based cavitation devices
 Symbols: experimental data; Lines: Euler number = 60.
 S: small cavitation device; L: large cavitation device (see Table 1 for other details)

The inception was found to occur when pressure drop across the cavitation device is just below 100 kPa. This is in agreement with the results reported by Gaikwad and Ranade (34). Similar inception

point was also observed for the case of a larger cavitation device. Attempts are being made to quantitatively and objectively identify inception point using the acquired acoustic signals. For this work, a qualitative and manual identification of inception was considered to be adequate since the focus was not on inception but on degradation performance of the cavitation reactor. In order to avoid any ambiguity, the operating range of pressure drop across the cavitation device for the present work was considered to be 150 kPa and above. In addition to flow rate through the main line, for each operating condition, flow rate through by-pass line was also measured. At 150 kPa, there is still a significant flow through by-pass line and therefore through a valve. With reasonable estimate of open area of the valve in the by-pass line at this operating condition indicated the cavitation number at the valve is slightly higher than 2. Considering that there may still be a possibility of some cavitation across the valve, even the data collected at 150 kPa pressure drop across the cavitation device was not considered in the further analysis (though it was used for estimating activation energy as shown in Figure 4). For unambiguous characterisation of the cavitation device, we have considered degradation performance data obtained at pressure drop values of 200 kPa and above.

The concentration profiles for different operating conditions (ΔP of 200 kPa to 350 kPa) are shown in Figure 7. It can be seen that influence of increase in pressure drop across cavitation device on degradation performance is not monotonic. The degradation performance was improved when pressure drop was increased from 200 kPa to 250 kPa. However, further increase in pressure drop across cavitation device was found to reduce degradation performance. Similar observations regarding existence of a maxima in degradation performance with respect to pressure drop has been reported in earlier works for conventional devices (26, 31, 32).

The experimentally measured concentration profiles were described very well by the per pass degradation model developed in this work (see comparison of predicted results shown by lines and experimental data in Figure 7). The fitted values of ϕ_0 are listed in Table 2. The variation of per pass degradation factor as a function of pressure drop is shown in Figure 8. It can be clearly seen that per pass degradation factor exhibits maxima at 250 kPa pressure drop across the cavitation device. The per pass degradation factor is proportional to G (generation rate of hydroxyl radicals) which in turn depends on product of number density of cavitation events and hydroxyl radicals generated per collapsing cavity. Higher pressure drop across the cavitation device generates more cavitation that is higher numbers of cavitation events. However, intensity of collapse of generated cavities decreases in presence of larger number of cavities. These two opposite effects of increase in pressure drop across cavitation device results into maxima in degradation performance with respect to the pressure drop.

Computational fluid dynamics (CFD) models can be used to relate pressure drop across the cavitation device and extent of cavitation. The CFD models can also provide information about the pressure history experienced by the cavities which can then be used with cavity dynamics models (35, 36) for estimating generation of hydroxyl radicals per cavity collapse. The framework developed here can thus be used along with the CFD and cavity dynamics models to understand influence of various design and operating parameters on degradation performance. The scope of this work however is restricted to present the per-pass degradation model and its application to treatment of solvent contaminated water. The framework and presented data will provide a sound basis for further work in this direction.

Figure 7: Influence of pressure drop on degradation performance
 Symbols: experimental data, and Lines: predictions using non-isothermal model with $\Delta E/R = 3950$ K.
 Pollutant: acetone, Total liquid volume: 0.0093 m^3

The degradation performance in terms of energy consumption per kg of pollutant removed is dependent on the ratio of per pass degradation factor and pressure drop (see Equation 6). The optimum performance therefore not necessarily coincide with the maximum degradation performance observed in Figure 8. The ratio of per pass degradation factor and pressure drop is shown in Figure 9. Considering that the per pass degradation factor will be zero up to cavitation inception (up to 100 kPa pressure drop across cavitation device), there exists an optimum pressure drop across cavitation device for maximising cavitation yield. The data collected in present work for different pollutants and two scales of cavitation device indicate that this optimum lies around 200 kPa. It may be worthwhile to investigate operation in the range from cavitation inception (100 kPa) to 200 kPa

provided that any other cavitation source within the flow circuit is unambiguously avoided. This was however not possible in the experimental set-ups used in this work.

Figure 8: Influence of pressure drop on per – pass degradation factor
Pollutant: acetone; S: smaller cavitation device; L: larger cavitation device
Values of ϕ were calculated at 300 K using values of ϕ_0 listed in Table 2 and Equation (10) with $\Delta E/R=3950$ K

Figure 9: Influence of pressure drop on effective cavitation yield ($\phi/\Delta P$)
S: smaller cavitation device; L: larger cavitation device; Values of ϕ were calculated at 300 K using values of ϕ_0 listed in Table 2 and Equation (10) with $\Delta E/R=3950$ K

4.4 Influence of aeration

As discussed in Section 1, aeration may enhance degradation performance of cavitation based treatment by providing additional source of nuclei, which might enhance the extent of cavitation. In this work, we evaluated influence of aeration on degradation of acetone. Air was sparged in the holding tank with a single tube sparger. The flow rates were set to 0.30, 1.01 and 1.46 vvm $[(L/min)_{\text{gas}}/L_{\text{liquid}}]$. The aeration was found to improve the degradation performance up to 1.01 vvm. Further increase in aeration rate appeared to reduce the per-pass degradation factor. The per pass degradation model was found to represent the observed experimental results quite well. The value of ϕ_0 obtained for different aeration rates are listed in Table 2. The per pass degradation factors at 300 K are shown in Figure 10. It can be seen that a small increase of 10% in ϕ was observed for 0.3 vvm aeration. Earlier study of Suryawanshi *et al.* (1) had reported a similar enhancement of approximately 10% for an aeration flow rate of 0.16 vvm. Increasing air flow rate to 1 vvm resulted in almost doubling of per pass degradation factor compared to that observed in absence of aeration. Further increase in aeration rate to 1.46 vvm showed a slight reduction in the per pass degradation factor. It is important to establish that observed increase in per pass degradation factor is indeed because of interaction of aeration and cavitation and not simply because of stripping caused by aeration. In order to establish this, aeration only experiments (without cavitation) were carried out to quantify the acetone removal via stripping. It was observed that after 3 hours of continuous stripping, acetone removed at the highest air flow rate (1.46 vvm) was 22%. The equivalent contribution to per – pass degradation factor was estimated from the concentration versus time profile for this case. At highest air flow rate of 1.46 vvm, the contribution of aeration to per – pass degradation factor was 0.0014 whereas the overall degradation factor for aeration and cavitation was more than 0.008. This clearly establishes that the observed enhancement in the per-pass degradation factor is because of higher effectiveness of cavitation (radical generation) in presence of aeration.

The high enhancement factors at higher flowrates may be attributed to the availability of additional reactive oxygen species, which are responsible for degradation reactions. Concentration of dissolved air will initially increase with aeration and therefore may enhance per-pass degradation factor. Beyond a limit, dissolved air may lead to more number density of cavities which may hamper collapse intensity. Thus, it is expected that increase in aeration rate beyond a certain value will cause per-pass degradation factor either plateau or reduce. Aeration appears to be a worthwhile pathway to enhance performance of hydrodynamic cavitation device.

Figure 10: Effect of aeration on degradation performance

Pollutant: acetone, Total liquid volume: 0.0093 m^3 ; ΔP : 250 kPa; Q : $8.08 \times 10^{-5} \text{ m}^3/\text{s}$; Values of ϕ were calculated at 300 K using values of ϕ_0 listed in Table 2 and Equation (10) with $\Delta E/R=3950 \text{ K}$

4.5 Influence of nature of pollutant

In order to understand influence of nature of pollutant on degradation performance (per pass degradation factor), experiments were carried with EA and IPA in addition to the acetone results discussed so far. The comparison of degradation performance of acetone, EA and IPA at 250 kPa pressure drop is shown in Figure 11. The experimental determination of ϕ at three different temperatures and two pressure drops for acetone degradation enabled the calculation of $\Delta E/R$ for the case of acetone as discussed earlier. Attempt was made to apply non-isothermal per pass degradation model discussed earlier using the same value of $\Delta E/R$ for other two pollutants. The simulated results are also shown in Figure 11. It can be seen that the non-isothermal model presented in this work was able to describe the experimental data very well. Thus, the temperature dependence of degradation of three pollutants studied in this work namely acetone, EA and IPA can be represented by the same value of $\Delta E/R$. Considering the similar nature of chemical species and likely intermediates this is not very surprising. Activation energy values may change for different types of chemical species like aromatics and will be investigated separately.

The degradation performance based on ϕ values, suggest that ethyl acetate degrades approximately 4 times faster than isopropyl alcohol and 1.5 times faster than acetone. In a treatment with hydrodynamic cavitation, pollutant degradation may occur by different pathways: it may occur inside the bubble (pyrolytic decomposition) or at the bubble-liquid interface or the bulk medium by diffusion

and reaction of radicals in the bulk (37). When pollutants are volatile and hydrophobic, pyrolytic decomposition may be dominant as observed in the case of chlorobenzene (37). All the three pollutants used in this study are hydrophilic. Therefore, the effective degradation performance is eventually dependent on relative reactivity of pollutant with hydroxyl radicals (either at the bubble – liquid interface or in the bulk liquid). There are numerous publications speculating on different possible reaction pathways towards complete mineralisation (for example, possible reaction pathways of mineralising acetone are discussed by Talukdar *et al.* (38)). Since in this work we have not analysed any of the intermediates and the developed per pass degradation model accounts only lumped reaction, no attempt was made to interpret observed differences in reactivity. The presented data will however be useful to design appropriate hydrodynamic cavitation based treatment for water contaminated with these three solvents.

Figure 11: Influence of chemical nature of pollutant on degradation performance
Operating conditions: $\Delta P = 250$ kPa; $Q = 8.08 \times 10^{-5}$ m³/s; $V = 0.0093$ m³.
(Symbols: experimental data, Curves: predictions by non-isothermal model using $\Delta E/R = 3950$)

4.6 Influence of pollutant concentration

There appears to be some confusion about influence of pollutant concentration on degradation performance of hydrodynamic cavitation process. A general so called ‘common sense’ based belief in industry is that higher concentration of the pollutant will improve the degradation performance. There are some reports in the published studies which indicate that degradation rates reduce with pollutant concentration (1). With this background, the per pass degradation model developed here indicates

that at small concentration of pollutant, the per pass degradation factor, ϕ , should be independent of pollutant concentration (Equation 9). We carried out experiments with different initial concentrations of acetone and IPA. The observed degradation performance was described very well with the per pass degradation model developed here. The values of per pass degradation factor at 300 K obtained at different initial pollutant concentration are shown in Figure 12. It can be seen that the per pass degradation factor obtained for acetone was constant up to 10000 ppm. For the case of 22000 ppm acetone, the per-pass degradation factor was increased somewhat. This may be because of vapour phase thermal degradation of acetone in collapsing cavities. For the case of IPA, the per-pass degradation factors were found to be independent of initial concentration at least up to 50000 ppm. The degradation performance in terms of cavitation yield (kg of COD/ kJ) will however improve with pollutant concentration (Equation 5) which is in line with the prevalent industry belief.

Figure 12: Influence of initial pollutant concentration

$\Delta P = 250$ kPa; $V = 9.3$ L; $Q = 8.08 \times 10^{-5}$ m³/s; Values of ϕ were calculated at 300 K using values of ϕ_0 listed in Table 2 and Equation (10) with $\Delta E/R=3950$ K

4.7 Influence of scale

Hydrodynamic cavitation has been proposed as a promising technology for wastewater treatment for quite some time (35). However, despite the significant number of patents and start-up companies, the technology is still not yet widely used in water treatment industry. The problems related to erosion and propensity to clogging associated with the conventional cavitation devices like orifice or venturi may be some of the reasons behind this lack of widespread use. However, lack of understanding and therefore a lack of systematic framework for design and scale-up might also restrict the applications

of hydrodynamic cavitation. We believe that the per pass degradation model presented in this work provides a basis for developing a systematic design framework for continuous wastewater treatment processes based on hydrodynamic cavitation. In order to develop such a framework, it is important to understand scale-up of cavitation devices. As mentioned in Section 1, unfortunately no systematic data or information is available on influence of scale on degradation performance of hydrodynamic cavitation. In this work, we have used geometrically similar vortex based cavitation devices at two scales. The ratio of characteristic dimensions of the considered cavitation devices was two. Thus the nominal capacity of the two devices was different by a factor of four. The pressure drop versus flow rate data was measured (see Figure 6). The characteristic flow curves for both the devices were represented very well by $Eu = 60$.

The degradation performance of acetone with the two cavitation devices is shown in Figure 13 for 250 kPa pressure drop. It can be seen that the degradation performance of a smaller device is significantly better than that of the larger device. The per pass degradation model developed in this work was able to describe the data on both the scales very well. The per pass degradation factors obtained for the larger device were smaller than those obtained with the smaller cavitation device (see Figure 8). The maxima in per-pass degradation factor with respect to pressure drop observed for the case of larger cavitation device was not found to be as pronounced as that observed for the smaller device.

Figure 13: Influence of scale on degradation performance.
Pollutant: Acetone; Pressure drop, $\Delta P=250$ kPa; S: $C_0=863$ ppm; L: $C_0=924$ ppm
(Symbols: experimental data, Curves: predictions by non-isothermal model using $\Delta E/R = 3950$)

It is important to understand the influence of scale more critically. Qualitatively from the data presented here (Figures 8, 9 and 13), the per-pass degradation factor, ϕ (or in other words, the generation rate of hydroxyl radicals, G) decreased with larger scale. The value of G is affected by extent of cavitation (number density of cavitation events) and intensity of collapse (hydroxyl radicals generated per collapsing cavity). Though the cavitation devices are geometrically similar and operated at same characteristic throat velocity, the extent of cavitation may change with the scale of the device. More importantly, intensity of collapse may also change with scale since pressure history and fluctuations experienced by cavities at two different scales may not remain same by just maintaining geometric and hydraulic similarity. Crucial understanding of cavitating flow in such devices coupled with trajectory simulations and prediction of collapse conditions (by cavity dynamics) are necessary to supplement the findings and complementing the reaction engineering model presented here. This work is in progress and will be published separately. The per pass degradation model and the data presented in this work will provide a sound basis for further work on developing systematic design and scale up guidelines for hydrodynamic cavitation based waste water treatment.

5. Conclusions

In this work, we have used vortex based hydrodynamic cavitation devices for treating solvent contaminated water. Three commonly used solvents namely acetone, EA and IPA were considered. A modelling framework based on a per-pass (through cavitation device) degradation factor is developed which provides a convenient way to connect with more sophisticated models (cavity dynamics and computational fluid dynamic models). Influence of scale of geometrically similar cavitation devices was investigated for the first time. The key conclusions from the study are as follows:

- Within the range investigated in this work (up to 318 K), increase in operating temperature was found to enhance degradation rates for all the considered pollutants. The influence of temperature on degradation rates was represented using the Arrhenius equation with $\Delta E/R=3950$ K.
- Per-pass degradation model developed in this work was able to describe the experimental data very well for all the three pollutants for all considered operating conditions.
- Per-pass degradation factor exhibited a maxima with respect to pressure drop (200 – 250 kPa) across the cavitation device.

- Aeration was found to enhance degradation factor up to a certain rate. Aeration rate of 1 vvm almost doubled the per-pass degradation factor when compared to that without aeration. Further increase in aeration beyond 1 vvm was found to decrease per-pass degradation factor.
- Per-pass degradation factor depends on the nature of the pollutant. The pollutant EA was observed to degrade approximately 4 times faster than acetone and 1.5 times faster than IPA.
- The degradation performance was found to be independent of initial concentration of the pollutant in the ranges of 1000 to 50000 ppm for IPA. At a concentration of 22000 ppm acetone, the per-pass degradation factor for acetone was found to be somewhat higher compared to that observed at low concentrations (less than 1%).
- The per-pass degradation factor was found to decrease with the scale of cavitation device. The smaller device (S) was observed to perform almost 5 times better than the larger device (L) across all operating pressure drops (ΔP).

The per-pass degradation model and the values reported here for different operating parameters as well as for two different scales of geometrically similar cavitation device provide a framework to understand and interpret degradation behaviour of pollutants. The framework enables a direct comparison of cavitation devices and facilitates extension to continuous operation. The models and results will be useful to researchers as well as practicing engineers interested in expanding application horizons of hydrodynamic cavitation for wastewater treatment.

Notations

b	Non-isothermal correction factor for piece-wise linear temperature profile, (-)
C	Outlet concentration for industrial cavitation setup ($\mu\text{mol}/\text{m}^3$)
C_0	Starting concentration of pollutants in experiments (ppm)
C_c	Critical concentration of pollutant ($\mu\text{mol}/\text{m}^3$)
C_{in}	Inlet concentration for industrial cavitation setup ($\mu\text{mol}/\text{m}^3$)
C_R	Concentration of hydroxyl radicals ($\mu\text{mol}/\text{m}^3$)
G	Generation rate of hydroxyl radicals (kmol/s)
k_0	Second order rate constant of reaction between hydroxyl radicals and other reactants than pollutant of interest ($\text{M}^{-1} \text{s}^{-1}$)
k_2	Second order rate constant ($\text{M}^{-1} \text{s}^{-1}$)
k_b	Apparent first order rate constant (s^{-1})
L	Large cavitating device with a nominal capacity of $1.2 \text{ m}^3/\text{hr}$
M_{wp}	Molecular weight of pollutant ($\text{kg}/\text{kg-mole}$)
n	Number of passes through cavitation device (-)
n_c	Number density of cavitation events ($\text{number}/\text{m}^3 \text{s}$)
q	Net flow in typical industrial cavitation setup (m^3/s)

Q	Recirculating flow through cavitation device (m ³ /s)
S	Small cavitating device with a nominal capacity of 0.30 m ³ /hr
T	Bulk temperature, (K)
V	Volume of holding tank (m ³)
v _t	Throat velocity (m/s)
Y	Cavitation yield (μg/J)
y _R	Number of hydroxyl radical generated per collapsing cavity (kmol/ cavity)
ΔE/R	Activation energy for pollutant, (K)
ΔP	Pressure drop across cavitation device (kPa)
ΔT	Change in temperature between consecutive number of passes, (K)
z _R	Stoichiometric coefficient
β	Ratio of flow rate through cavitation device (Q) and holding tank volume (V) (s ⁻¹)
φ	Per-pass degradation factor (-)
φ ₀	Per-pass degradation factor, analogous to Arrhenius factor (-)
φ _{0,avg}	Per-pass degradation factor evaluated for non-isothermal condition (-)
φ _C	Critical per-pass degradation factor for pollutant (-)
ρ	Density of liquid (kg/m ³)
τ	Residence time of liquid in holding tank (s)
τ _R	Life time of hydroxyl radicals (s)

Acknowledgements:

Authors gratefully acknowledge the funding support from the start-up grant G1013CHM of Queen's University Belfast, UK as well as Invest NI CASE project CAVICAT (R3947CCE).

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