Quantifying OH radical generation in hydrodynamic cavitation via coumarin dosimetry: Influence of operating parameters and cavitation devices

Sebastien J. De-Nasri\textsuperscript{a,} , Varaha P. Sarvothaman\textsuperscript{a,} , Sanjay Nagarajan\textsuperscript{a,\textsuperscript{b,}} , Panagiotis Manesiotis\textsuperscript{a,} , Peter K.J. Robertson\textsuperscript{a,} , Vivek V. Ranade\textsuperscript{a,\textsuperscript{c,\textsuperscript{x}}}

\textsuperscript{a} School of Chemistry and Chemical Engineering, Queen’s University Belfast, Belfast BT9 5AG, UK
\textsuperscript{b} Sustainable Environment Research Centre, University of South Wales, Pontypridd CF37 1DL, UK
\textsuperscript{c} Bernal Institute, University of Limerick, Limerick, Ireland

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\textbf{A B S T R A C T}

Hydrodynamic cavitation (HC) has been extensively investigated for effluent treatment applications. Performance of HC devices or processes is often reported in terms of degradation of organic pollutants rather than quantification of hydroxyl (OH) radicals. In this study, generation of OH radicals in vortex based cavitation device using coumarin dosimetry was quantified. Coumarin was used as the chemical probe with an initial concentration of 100 \( \mu \text{M} \) (15 ppm). Generation of OH radicals was quantified by analysing generated single hydroxylated products. The influence of operating parameters such as pH and type of acid used to adjust pH, dissolved oxygen, and inlet and outlet pressures was investigated. Acidic pH was found to be more conducive for generating OH radicals and therefore subsequent experiments were performed at pH of 3. Sulphuric acid was found to be more than three times effective than hydrochloric acid in generating OH radicals. Effect of initial levels of dissolved oxygen was found to influence OH radical generation. Performance of vortex based cavitation device was then compared with other commonly used cavitation devices based on orifice and venturi. The vortex based cavitation device was found to outperform the orifice and venturi based devices in terms of initial per-pass factor. Influence of device scale (nominal flow rate through the device) on performance was then evaluated. The results presented for these devices unambiguously quantifies their cavitational performance. The presented results will be useful for evaluating computational models and stimulate further development of predictive computational models in this challenging area.

\textbf{1. Introduction}

Cavitation is the formation, growth, and collapse of gas filled cavities in a liquid. The collapse of cavities give rise to physicochemical transformations by introduction of intense shear and generation of hydroxyl (OH) radicals. Out of various ways of realising cavitation, hydrodynamic cavitation (HC) is amenable to scale-up and relevant for industrial processes in areas such as water treatment, pre-treatment of biomass and water disinfection among others \cite{1}. In an attempt to consolidate the studies to compare different devices, Sarvothaman et al. \cite{1} used five device types exhibiting similar pressure drop versus flow curve. By doing so (using devices of a similar flow curve), a comparable power consumption was...
Dosimetry studies in hydrodynamic cavitation are a subset of research towards advanced oxidation processes, which are aimed at establishing evidence of hydroxylation. Advanced oxidation processes (AOPs) are processes which can generate OH radicals sufficient to mineralize pollutants in a wastewater stream. Typically, such studies comprise the use of potassium iodide [Weissler reaction], iron sulphate [Fricke dosimetry], salicylic acid, terephthalic acid or coumarin dosimetry [16–18]. These methods although employing different initial chemical reactants, in principle rely on the reaction between the initial reactant as a scavenger for OH radicals formed in the hydrodynamic cavitation process. The relationship of hydroxyl radicals and degradation of organic pollutants has been established and discussed extensively in published studies on hydrodynamic cavitation (for example: Sarvothaman et al. [19]; Capocelli et al. [20]; Pawar et al. [21]). In our earlier work (Sarvothaman et al. [19]; Ranade et al. [22]), we have shown the relationship between the per-pass degradation factor ($\phi$) is directly proportional to the hydroxyl radicals generation rate, G. It is therefore important to quantify hydroxyl radical generation rate unambiguously. In this work, such measurements in the form of quantified hydroxylation were carried out using coumarin as a chemical probe.

For a given chemical probe, it is important to choose operating conditions such as operating pH (evaluate the possibility of chemical reagents influencing the cavitation process) and the role of dissolved oxygen, and thereby quantify their influence on hydroxylation. Operating pH influences the hydroxylation dependent on the solute. If a solute is present in a dissociated form (ionic), the hydroxylation is relatively lower to that of when it is present in its molecular form [10,23]. A recent study which used multiple phenolic compounds in the presence of different mineral acids as the pH modifier concluded that the type of mineral acid plays a significant role in the cavitation performance [24]. Apart from the pH effects, the next most important parameter is the role of dissolved gas. The dissolved gas influences the cavitation in two ways, the first is to modify the inception of cavitation and the second is to alter the intensity of cavity collapse. The variation of dissolved gases has been commonly researched in acoustic cavitation and the second is to alter the intensity of cavity collapse. The variation of dissolved gases has been commonly researched in acoustic cavitation and the second is to alter the intensity of cavity collapse. The variation of dissolved gases has been commonly researched in acoustic cavitation literature [25]. A general understanding is that oxygen saturation promotes the process performance. However, the quantification or the sensitivity of this is not reported in hydrodynamic cavitation literature. Apart from these observations on operating parameters: more often than not, the data from hydrodynamic cavitation literature is presented with respect to time rather than number of passes, when indeed cavitation performance is a function of number of passes [12,19].

In this work, the influence of pH, pressure ratios (inlet and outlet/downstream pressures), and dissolved oxygen on hydroxylation in a vortex-diode based cavitation device using coumarin as a chemical probe was studied.
probe was investigated. The nominal capacity of the cavitation device was 5 LPM (with a characteristic dimension of \( d_t = 6\text{-mm} \), device D1). Coumarin was chosen as a chemical probe due to its solubility in water and that its hydroxylated product (7-hydroxycoumarin) can be easily quantified on the fluorescence spectra [26]. The optimal operating conditions identified on device D1 were used to quantify hydroxylation on different device types (devices D2 – D6), and two higher scale of cavitation devices (D2 and D7). The detailed flow characteristics of cavitation devices used in the study have been reported earlier by Simpson and Ranade [4,27–29]. The approach of using well characterized cavitation devices and quantification of direct cavitation effects will provide a better understanding and sound basis for the selection and scale-up of hydrodynamic cavitation devices. The key results are discussed after presenting details of the experimental set-up and methods.

2. Materials and methodology

The discussion is grouped into three sub-sections: the first was the experimental rig to operate the different cavitation devices in the study, the subsequent discussion was on the reagents used and the following one details the analytical method to quantify concentration of the reactants and products.

2.1. Experimental set-up and considered HC devices

Two experimental setups/configurations were employed in this study. We used the first configuration, i.e. a setup identical to that of Sarvothaman et al. [19] (schematic presented in Fig. 2) for six out of seven devices in the study. In an ideal case, it is desired to operate the cavitation setup without a bypass line, in order to avoid a possibility of extraneous sources of cavitation [19]. In the case of the first cavitation device (vortex diode with \( d_{t} = 6\text{-mm} \) – device D1, refer Table 1), it was operated with a bypass line to ensure that most of the devices were operated on the same experimental setup. Care was taken to ensure that there was no cavitation anywhere else in the experimental flow loop except in the considered cavitation device [19,30]. Devices D1 – D6 were operated on the first experimental setup (for details on devices, refer Table 1) and a higher capacity device D7 (flowrate of 227 LPM at 280 kPa; vortex diode with \( d_{t} = 38\text{-mm} \)), was operated in a second experimental setup. The details of this second experimental configuration can be found in one of our earlier works – Ranade et al. [12].

The pressure drop versus flow curves for most of the devices used here have been reported in the work of Ranade et al. [12] and Sarvothaman et al. [1], and hence are not included here for the sake of brevity. The data on flow rates through cavitation devices measured over the pressure drop range of 50 to 350 kPa across the three scales have been presented in our earlier studies [1,12]. The other device types such as orifice (D3), orifice with swirl (D4) and the venturi (D5) have a similar pressure versus flow curve to that of the vortex diode device (D2) [1,4]. The rounded orifice device (D6) was deliberately chosen to employ a device with a dissimilar flow curve to that of devices D2 – D5 (the flow curves for devices D2 to D6 are presented in SI Fig. S1).

2.2. Chemicals used

Coumarin and 4-Hydroxycoumarin were obtained from Acros organics, 3-Hydroxycoumarin, 3-(2-Hydroxyphenyl) propionic acid, and 7-hydroxycoumarin (7OH) were obtained from Sigma-Aldrich, trans-o-Coumaric acid was obtained from Tokyo chemical Industry Co., and 6-Hydroxycoumarin was obtained from Fisher scientific. All chemicals had purities of 98 % or higher. Methanol (\( \geq 99.8 \% \)) and acetic acid (\( \geq 99.8 \% \)) were procured from Fisher Scientific and Sigma Aldrich, respectively. All chemicals were used as received. Stock solutions of coumarin (8.2 mM) and its products (100 \( \mu \text{M} \)) were prepared to their desired concentration and diluted using distilled water when required. Calibration curves for each chemical were prepared using their associated stock solution and analysed using high performance liquid chromatography (HPLC). HPLC mobile phases were prepared using deionised water. The initial concentration of coumarin for this study was 100 \( \mu \text{M} \) (15 ppm), as followed in our previous study pertaining to dosimetry [26].

2.3. Analytical techniques

Sample analysis was performed using HPLC. An InifinityLab Poroshell 120 Phenyl Hexyl column was used for this purpose. A mobile phase flow rate of 1 mL/min was used. A solvent gradient between two mobile phase solutions; solvent A and B (solvent A: 89 % de-ionised water, 10 % methanol and 1 % Acetic acid, Solvent B: 89 % methanol, 10 % de-ionised water and 1 % Acetic acid) was used to mobilise the samples through the stationary phase. A linear flow gradient from 90 % A, 10 % B (run-time = 0 min) to 40 % A, 60 % B (run-time = 10 min) and a temperature of 30 °C (maintained using an Agilent G1316A column compartment) gave the most effective separation between components. An additional 3 min run-time was added to flush the column between runs. 5 \( \mu \text{L} \) sample volume was injected into the column using an Agilent G1313A autosampler. The samples were analysed using an Agilent G7121A 1260 infinity II Fluorescence Detector (excitation wavelength:

![Fig. 2. Schematic of experimental set up (Sarvothaman et al. [19]).](image-url)
Table 1
Details of experimental setup and cavitation devices used in this study.

| Device name | Device type | Throat diameter of cavitation device (mm) | Window of inception ΔP (kPa) | Pump details | Frequency controller installed | Inlet pressure – P₁ for coumarin hydroxylation experiments (kPa gauge) | By pass flow during experiments | Liquid volume (L) |
|-------------|-------------|------------------------------------------|-----------------------------|--------------|-------------------------------|---------------------------------------------------------------|-----------------------------|-----------------|
| D1          | Vortex diode | 6                                       | 50 – 80                     | Grundfos CM 1 – 5 | No                            | 100 & 200                                                    | X                           | 4.5             |
| D2          | Vortex diode | 12                                      | 50 – 80                     | ''            | ''                            | 200                                                           | X                           | 6               |
| D3          | Orifice     | 5                                       | 80 – 90                     | ''            | ''                            | 200                                                           | X                           | 6               |
| D4          | Swirler + Orifice | 5 | 70 – 80                     | ''            | ''                            | 200                                                           | X                           | 6               |
| D5          | Venturi     | 4                                       | 50 – 60                     | ''            | ''                            | 200                                                           | X                           | 6               |
| D6          | Rounded Orifice | 5 | 140 – 160                   | ''            | ''                            | 200                                                           | X                           | 6               |
| D7          | Vortex diode | 38                                      | 50 – 80                     | Lowara – SHOE 32 – 200/30/D | ''            | 280                                                           | X                           | 80              |

332 nm, emission wavelength 450 nm) for 7OHC, and an Agilent 1100 HPLC G1315B DAD Detector (signal wavelength: 277 and 325 nm) for coumarin and other products. Calibration curves were used to determine their relative concentrations during experiments (SI Fig. 2). The concentration obtained from experiments were interpreted with respect to number of passes through the cavitation device, more information on the rationale for using the reaction engineering framework is available in the work of Ranade et al. [12], the approach used for this article is provided in the supplementary information. Experiments were performed in duplicate, concentration profile of both experiments were used to calculate the initial per-pass coefficient detailed in supplementary information (see Section SI – C and Table S1).

3. Results and discussion

The basic characteristics of a cavitation device and the experimental setup on which it is operated are the device flowrate, device inception window, pump specifications and operating volume. These have been listed in Table 1 for the devices used in the study.

3.1. Influence of pH and acid type

Solution pH is a parameter which can significantly influence the cavitation process. When the solution pH > pKᵣ of the pollutant species, the pollutant exists in its dissociated (ionic) form, otherwise it exists in an undissociated (molecular) form. The ionic form of the compound tends to remain in the bulk solution making it less prone to exposure to the oxidation by OH radicals formed by cavitation. When the compound exists in the molecular form, it accumulates at the cavity interface and therefore is more susceptible to oxidation by OH radicals [10,31]. For instance, Capocelli et al. [23] reported that decreasing pH from 8 to 5.5 increased the removal of p-Nitrophenol by nearly 3 times. In a study of degradation of diclofenac sodium, Bagal and Gogate [32] reported that the decreasing pH from 7.5 to 4, doubled the rate of degradation. These studies are representative of acidic pH improving the oxidation by OH radicals/cavitation performance. When multiple functional groups are present – such as that of ibuprofen or tetracycline, Musmarra et al. [33] and Wang et al. [34] have shown that the pH does not play a part in improving cavitation performance. In the case of coumarin dosimetry studies, a previous study aimed to study the optimum conditions for hydroxylation in vortex diodes of which the investigation of pH was a part. In the study, however, the upper limit of degradation (conversion) of coumarin was 5%, which is insufficient to provide any firm understanding [35]. The pKᵣ of coumarin has been reported to be 4.2. In the study [35], across a pH range of 2 – 8.2, the highest removal was obtained at pH of 3 (~4% degradation) and decreasing to value of 2 did not increase the degradation further.

In the current study, the degradation of coumarin was studied at pH conditions of 3, 7 and 10. At all these three operating conditions, the concentration of coumarin and 7-hydroxycoumarin were quantified (plotted in Fig. 3). It was observed that at pH values of 3 and 7, the coumarin decreased by about 8% in 175 passes (Fig. 3 a). However, in the profile of 7-hydroxycoumarin, it can be observed that at pH value of 3, there is formation of 7-hydroxycoumarin, and this could not be observed at the pH value of 7 (Fig. 3 b). At pH 10, the routine analysis applied seemed to have interferences, possibly due to alkali addition. Operating at a basic pH (10), far from the pKᵣ (4.2) is not expected to beneficially enhance the process, hence the basic pH was not considered for further experiments. Among the operating conditions of pH 3 and 7, as it was possible to observe formation of 7-hydroxycoumarin at pH 3, this was considered for subsequent experiments. In our experiments: standards of coumarin and its possible reaction products were calibrated on the analytical method. It was possible to monitor only one hydroxylated species – 7-hydroxycoumarin. Since the interest was to quantify cavitational activity (hydroxylation), it was sufficient to quantify 7-hydroxycoumarin alone.

The possibility of increasing pollutant degradation, by contribution of anions to the radical generation in cavitation process was illustrated by Gagol et al. [24], wherein the degradation of multiple phenolic species was enhanced in the presence of H₂SO₄, but not so in the case of HCl. It was decided to test whether this change in mineral acid impacts hydroxylation. Hence, we swapped the mineral acid in our study, the results of this experiment: the 7-hydroxycoumarin formation are presented in Fig. 4.

It was observed that H₂SO₄ does aid in effecting higher degradation of coumarin, and reflected in the 7-hydroxycoumarin formation, wherein this tripled over 190 passes. Sulphate radicals have higher oxidation potential than chloride radicals (2.6 eV [36] and 1.36 eV [37], respectively). In a recent review on strategies of improving phenol degradation using cavitation based processing, the authors discuss the applicability of persulphate ions to form sulphate anions for effective oxidation [38]. Performance with H₂SO₄ may therefore be higher than that with HCl. Despite better performance of H₂SO₄, considering the lower cost, HCl was used for further experimentation.

3.2. Influence of DO

The dissolved gas (oxygen) is a process parameter which can affect the cavitation bubble formation in two ways: The first is that it alters the composition of the gaseous contents of the bubble at its inception and thereby the species at the collapse of the bubble. The second aspect is that it alters the transport properties like thermal conductivity, and thereby the severity of the hot spot formation [39]. As a result of these two factors, the hydroxylation is expected to be altered at different dissolved gas (oxygen) concentrations. There has been significant work in terms of acoustic cavitation, were the use of Argon/Helium/Nitrogen/Carbon dioxide have been tested experimentally and numerically.

Rooze et al. [25] reviewed the use of different gas atmospheres for...
acoustic cavitation based water treatment. They noted that there was no definitive trend favouring the use of one over the other, for over 15 aromatic pollutants. In the case of hydrodynamic cavitation, the altering of gas atmosphere is relatively uncommon. Suslick et al. [40] studied the Weissler reaction, i.e. the monitoring of tri-iodide formation at different ratios of Argon and Helium. They quantified the effect of varying Argon-Helium ratio and observed a five time increase in tri-iodide formation rate with pure Argon atmosphere as against Helium atmosphere. In a study of phenol degradation, Wu et al. [41] varied the gas atmosphere with nitrogen and oxygen, and compared it with their baseline conditions. Of the five datasets presented, the sparging of nitrogen (0.05 L/min N₂, in 70 L) was the only one which seemed to alter the degradation of phenol, lowering it from 22.5 to 15 % in 90 min. In other studies, such as those of Suryawanshi et al. [42] and Sarvothaman et al. [19], the authors used aeration as means to enhance the removal of solvent contaminated water. Sarvothaman et al. [19] used aeration between 0.3 and 1.4 vvm, and noted that aeration above 1 vvm was detrimental to degradation. Due to excessive concentration of gas bubbles, the compressibility of the vapour-liquid medium was lowered and hence this led to a cushioned collapse of bubbles, thereby lowering hydroxylation. In all the above studies pertaining to alteration of dissolved gas media, there has been no attempt to relate the dissolved oxygen to the hydroxylation.

To address this and quantify the effect of dissolved oxygen on hydroxylation, in the current study, there were three experiments designed: in the first experiment, no alteration of the dissolved medium was attempted for a baseline testing. In the second and third experiment, dry-ice was added to the liquid. This was a crude attempt to strip the dissolved oxygen. The dissolved oxygen was monitored throughout the treatment time (Fig. 5a). From the profiles of dissolved oxygen, it can be
seen that the saturation conditions were maintained throughout the first experiment. Whereas in the second experiment, an attempt was made to take the initial level of dissolved oxygen concentration (DO$_0$) close as 1 ppm. And in the third experiment, an attempt was made to take this initial level of dissolved oxygen concentration (DO$_0$) as 3.5 ppm. The corresponding 7-hydroxycoumarin concentration profiles are plotted in Fig. 5 b.

In the case of the two experiments where dry ice was added: in the experiment where the DO$_0$ was 1 ppm, the formation of 7-hydroxycoumarin was not observed after nearly 60 passes. In the experiment where the DO$_0$ was 3.5 ppm, such a lag was not observed. At the end of the experiments, the 7-hydroxycoumarin was comparable for both these dry ice based experiments and the 7-hydroxycoumarin was halved when compared to baseline conditions (experiment where DO$_0$ was not altered). More systematic experiments are required to relate the per-pass coefficient to the dissolved oxygen. The presented data, however, explicitly relates the dependence of dissolved oxygen for hydroxylation, which is otherwise not presented in hydrodynamic cavitation literature. On establishing that dissolved oxygen was a required operating parameter, the baseline testing (experiment where DO$_0$ was not altered) was chosen for further experimentation.

### 3.3. Influence of pressure

The cavitational performance in a cavitation device can be manipulated by adjusting either the inlet or outlet/downstream pressure. As long as there is a sufficient driving force for cavitation, hydroxylation can be expected. Table 1 lists the inlet pressure window at which inception of cavitation was reported for the cavitation devices used in this study. The device D1 was chosen for this investigation. Previous studies which used this device (D1: vortex diode with d$_i$ = 6-mm) reported the removal of acetone [19] and dichloroaniline [12]. In these studies, the influence of pressure drop was found to be negligible and hence implied that the lowest operating pressure drop was suitable for the removal of organic pollutants. In this study, it was decided to compare the inlet pressure at two conditions ~200 and 100 kPa gauge. From Table 1, it can be noted that the 100 kPa gauge condition is beyond the inception of cavitation for this device. In Fig. 6 a, the initial per-pass degradation is plotted for these inlet pressure values, this indicates a nearly 7 times superior removal at the lower inlet pressure condition. At a comparable treatment duration (~155 passes), it can be observed that the 7-hydroxycoumarin formation (Fig. 6 b), is 4 times superior for the 100 kPa gauge when compared to the 200 kPa gauge inlet pressure (SI Table 1). This result suggests that the vortex diode is sensitive to inlet pressure and a more detailed study on inlet pressure conditions for different scales of vortex diode could be investigated for optimizing cavitational activity.

The next device parameter which can influence pressure ratio is the outlet/downstream pressure of the cavitation device. At a given inlet pressure, increasing the downstream pressure can increase the cavitational activity up to a finite value (Soyama and Hoshino, [43]). After which the cavitational activity reduces and finally ceases to exist when the sufficient pressure drop is not available to initiate cavitation. There have been reports to increase the pollutant removal using downstream pressure as a tool [30,44]. There have, however, been no studies to quantify the hydroxylation or direct chemical effects. In this study, the gauge pressures for the inlet and downstream pressures were maintained as 200 (P$_1$) – 0 kPa (P$_2$) and 200 (P$_1$) – 100 kPa (P$_2$). By studying this pair, it was possible to observe that the initial per-pass degradation was enhanced by nearly 3 times when P$_2$ was elevated (set at 100 kPa). The corresponding enhancement in the 7-hydroxycoumarin formation was 2.3 times.

Overall degradation performance of hydrodynamic cavitation process is a function of extent of cavitation (in other words, number of cavitation events) and intensity of cavitation events (in other words, generated physico-chemical effects due to collapsing cavities). The extent of cavitation depends on the generation of low-pressure zone within the device, which in turn depends on characteristic velocity in the device (throat velocity) as well as on the inlet pressure. Cavities generated at the low-pressure region eventually collapse as they travel to high pressure regions. The pressure gradient (difference between the lowest pressure generated in the device and pressure at the outlet) experienced by cavities determine intensity of collapse. Since these two factors are inter-related in a complex, non-linear way, it is not possible to relate the observed performance with operating conditions with a simple explanation. Detailed computational fluid dynamics models are usually necessary to quantitatively understand differences in performance at different conditions (see for example, Sarvothaman et al. [30]). However, these enhancement values corroborate the previous investigations of downstream pressure and unambiguously proves that the enhancement in pollutant degradation is by hydroxylation effects in vortex diode-based cavitation devices.

![Fig. 4. Influence of acid-type on 7-hydroxycoumarin formation using with Device D1 at P$_1$ = 200 kPa gauge, T = 18 ± 2 °C.](image-url)
Upon quantifying these different parameters influencing the cavitation process, it is important to understand how temperature plays a role on the hydroxylation process. The hydroxylation process depends on the intensity of cavitation, which in turn depends on the temperature of the process liquid (for a given operating condition and cavitation device). There is an optimum range of temperature at which hydroxylation activity is expected to be maximum (Sarvothaman [39]). The data for the influence of temperature on a specific solute, such as that of coumarin would be specific to this study and hence this was not gathered. In one of our earlier works (Sarvothaman et al. [19]), we have presented a per-pass modelling framework for simulating role of temperature on HC performance which may be used develop appropriate operating strategies.

As a next step, the different cavitation devices were compared.

3.4. Influence of device type

The comparison of different device types for optimizing cavitational yield has been the subject of research in different applications such as wastewater treatment and emulsification [7,45,46]. As previously discussed, studies in prior literature have used devices at a constant pressure drop and discuss no basis for this [1]. Sarvothaman et al. [1] have used cavitation devices with a comparable power consumption, by ensuring they have a similar pressure versus flow curve. Their study, however, used dichloroaniline, an aromatic pollutant and quantified its removal alone. In this study, the devices used in their study are employed (devices D2/D3/D4/D5). Apart from this a rounded orifice (D6) with a dissimilar flow curve to the devices D2/D3/D4/D5, this device D6 exhibited a 1.2 time increase in flowrate at 200 kPa gauge. The experiment was performed at an inlet pressure of 200 kPa and the

![Fig. 5. Influence of DO on – a) dissolved oxygen and b) formation of 7-hydroxycoumarin Device D1 at P₁ = 200 kPa gauge, T = 18 ± 2 °C.](image-url)
The initial degradation is presented as Fig. 7a. It can be observed that the vortex diode based device exhibited the higher removal per unit energy expense ($811 \pm 144 \mu g/hr/W$). The initial degradation for the other devices: orifice (D3), venturi (D4) and orifice with swirl (D5) are $241 \pm 27 \mu g/hr/W$, which was 0.3 times lower than that of the vortex diode with comparable energy dissipation. By using a rounded orifice with a dissimilar flow curve (D6), the initial degradation was 1.76 times that of devices D3/D4/D5 and 0.52 times that of device D2 (vortex diode with $d_t = 12$-mm).

Although the initial degradation suggests superiority of device D2 (vortex diode with $d_t = 12$-mm) over device D6 (orifice with dissimilar flow curve), on examining the 7-hydroxycoumarin concentration profile (Fig. 7b), it can be observed that they have comparable levels 7-hydroxycoumarin formation. On a closer look at this figure, one can point that the device D2 starts removing 7-hydroxycoumarin roughly after 350 passes. However, this is not the case with device D6 (rounded orifice). Considering that for water treatment type of applications, the overall removal is more important, it can be said that device D2 (vortex diode with $d_t = 12$-mm) is superior to that of device D6 (rounded orifice) by considering the removal per unit energy expense and secondly the 7-hydroxycoumarin removal.

Based on the results of the initial degradation obtained, it indicates that the orifice (D3), venturi (D4) and swirl orifice (D5) exhibited a comparable chemical performance within themselves and also that swirl does not suppress the chemical performance. On the other hand, the use of rounded orifice (D6) – device with a higher flowrate and hence a dissimilar Euler number showed a 1.76 time increase in degradation per...
unit energy expense. Suggesting that dissimilarity of the flow curve in linear devices and their variants might lead to different cavitation performance. The cavitation yield (Saharan et al. [47]) was calculated for these devices and is presented in SI Table S1. The cavitation yield showed a similar trend to the per-pass degradation. More detailed investigation on pressure ratios and other characterization can be the subject of further research for these unique cavitation devices.

3.5. Influence of scale

One of the significant advantages and the premise for investigating hydrodynamic cavitation is its scalability [11,48]. Only a handful of studies, however, have reported the influence of the influence of scale of cavitation devices. Similar to the investigation of different device types, the pollutants for the influence of scale used dichloroaniline as a pollutant for their investigation [12]. The results of the study pointed that the process performance deteriorated with increase in scale and developed a correlation between performance and scale. The results from coumarin hydroxylation and 7-hydroxycoumarin formation are presented in Fig. 8. The inlet pressure condition for device D1 (d_t = 6-mm), device D2 (d_t = 12-mm) and device D7 (d_t = 38-mm) were 200, 200 and 280 kPa gauge respectively. Due to constraints on the existing pump used to operate device D7, unfortunately device D7 was operated at a dissimilar inlet pressure condition. The concentration profile of coumarin is shown in Fig. 8 a. The largest scale of device (d_t = 38-mm/ device D7) shows rapid initial removal (up to 50 %) in 175 passes.

Fig. 7. Influence of cavitation device type at on a) initial degradation and b) 7-hydroxycoumarin formation, at P_1 = 200 kPa gauge and T = 18 ± 2 °C.
However, the removal of coumarin did not continue beyond this point. This is also confirmed by the 7-hydroxycoumarin formation (Fig. 8 b), which seemed to plateau in similar treatment duration.

For the intermediate scale of device ($d_t = 12$-mm/device D2), this showed a removal of 85% in 600 passes without any deceleration in coumarin removal. Further the 7-hydroxycoumarin formed was consumed between 380 and 650 passes. In the case of the smallest scale of device ($d_t = 6$-mm/device D1), the removal was 10% in 190 passes, which is inferior to the removal on the two higher scales of operation. Increasing the performance on the smallest scale: the investigation on downstream pressure, showed that elevating $P_2$ to 100 kPa increased removal by 3 times (supplementary information: SI Table 1). Additionally, lowering the inlet pressure 100 kPa increased the initial per-pass removal by 7.3 times. These results collectively show that influence of scale was not detrimental, and manipulation of device pressure parameters were sensitive, to process performance. These results of hydroxylation of coumarin spanning a considerable scale of cavitation device operation and providing results of scale-up and inlet pressure will be useful for validation of computational models as well as for implementation of hydrodynamic cavitation for wastewater treatment applications.

4. Conclusions

Coumarin was employed as a chemical probe and the formation of 7-hydroxycoumarin, a fluorescent product for quantifying generation of OH radicals, monitored. Influence of operating parameters such as pH, acid type and dissolved oxygen was investigated on a vortex based cavitation device with nominal flow rate of 5 LPM (throat diameter of 6 mm). Generation of OH radicals in different device types and scales was
then quantified and compared. The experimental results were discussed using a per-pass modelling framework, coumarin conversion and the formation of 7-hydroxycoumarin. The key conclusions from the study are summarized as follows:

- Acidic pH (3) was necessary to observe formation of hydroxylated products
- Using H2SO4 instead of HCl to modify pH, the initial per-pass constant was 7 times superior and 7-hydroxycoumarin formed at identical number of passes (192) was 3.25 times higher
- Dissolved oxygen had a direct impact on hydroxylation, ~ 30 % decreased 7-hydroxycoumarin formation was observed when DO was 1 and 3.5 ppm as compared to an operation where the initial level (DO) and levels throughout the treatment were at saturated (11.5 ppm) conditions
- Vortex diode device with d = 6-mm was sensitive to inlet pressure, decreasing inlet pressure from 200 to 100 kPa gauge increased initial per-pass constant by 7.3 times
- Vortex diode device with d = 6-mm was sensitive to downstream pressure, elevating downstream pressure by 100 kPa, increased initial per-pass constant by 3 times
- Using devices of comparable power consumption, vortex-diode outperformed the orifice/orifice-with-swirl and venturi devices, by 3 times based on initial per-pass constant
- Using a rounded orifice device (with 1.2 times higher consumption) the initial per-pass constant was 1.7 times that of the orifice-orifice-with-swirl and venturi devices
- On comparing 3 scales of vortex diode (nominal flow rates of 5 [d = 6], 20 [d = 12-mm] and 250 LPM [d = 38-mm] – i.e., a scale-up factor of 50 at dissimilar pressure drop (200, 200 and 280 kPa respectively), it was observed that scale-up was not detrimental to hydroxylation

The available results of scale-up not being detrimental is encouraging for expanding applications of these devices for wastewater treatment applications, either stand-alone or with hybrid technologies. The results will be useful to researchers as well as practicing engineers in expanding the application of hydrodynamic cavitation for effluent treatment.

CRediT authorship contribution statement

Sebastien J. De-Nasri: Investigation, Data curation, Validation, Writing – original draft. Varaha P. Sarvothaman: Investigation, Methodology, Data curation, Validation, Writing – review & editing. Sanjay Nagarajan: Methodology, Validation. Panagiotis Manesiotis: Methodology, Supervision. Peter K.J. Robertson: Supervision, Writing – review & editing. Vivek V. Ranade: Conceptualization, Funding acquisition, Supervision, Writing – review & editing.

Declaration of Competing Interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Vivek Ranade reports a relationship with VIVIРА Process Technologies that includes: board membership.

Data availability

Data will be made available on request.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.ultraschon.2022.106207.

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