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Quantification of Hydroxyl Radicals in Photocatalysis and Acoustic Cavitation: Utility of Coumarin as a Chemical Probe

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Abstract

In-situ hydroxyl radical production is a characteristic of advanced oxidation processes (AOPs) and its quantification is crucial for assessing the performance of these processes. Direct OH quantification is however unlikely due to their high reactivity and short life-time ($\sim 10^{-6}$ s). Therefore, chemical probes (like coumarin) are often used to indirectly quantify OH radicals. The resulting hydroxylated products of these probe molecules are relatively stable and detectable (like 7-hydroxycoumarin; 7OHC); their concentration is usually related to the OH radical concentration. Reported literature suggests the use of a constant fraction (6.1 %) as the yield of 7OHC from total OH radicals generated (δ). This was originally determined from γ -irradiation studies of coumarin and translated across to other AOPs. It is however highly unlikely that this fraction is same across other AOPs. To address this gap and as a means of comparing AOPs, in the present work, we used coumarin as a probe to quantify 7OHC during acoustic cavitation (AC) and photocatalysis (PC) and determined the OH radical yields. Since δ cannot be determined directly, an alternative and simple means of comparison based on the amount of OH radicals utilised for desired reactions i.e., hydroxylation was exploited. Based on the proposed means of comparison, it was determined that OH radicals utilised by the probe was higher for PC than AC by ~ 25 times under the considered process operating conditions. The presented results will be useful for researchers and engineers interested in quantifying hydroxyl radicals and optimising AOPs.

Key words: Hydroxyl radicals, coumarin, cavitation, photocatalysis, quantification

1. Introduction

The role of advanced oxidation processes (AOPs) in the wastewater treatment industry has been examined extensively in recent years [1–3]. This is attributed to their ability to remove pollutants resistant to conventional treatment [4]. A defining characteristic of AOPs is their in-situ generation of oxidising radicals such as hydroxyl (OH) radicals. Although numerous radical species are reported, OH radicals are frequently assigned as the major species responsible for the oxidation of compounds due to their strong oxidation potential of 2.8 V[1,5]. Cavitation and photocatalysis are two attractive AOPs which have gained attention in wastewater treatment applications due to their applicability to a range of pollutants and synergistic operations[6–12]. Acoustic cavitation (AC) is the formation and subsequent collapse of vapour filled cavities using ultrasonic waves which generate localised hotspots that lead to the formation of OH radicals. On the other hand, during photocatalysis (PC), when a semiconductor photocatalyst is illuminated with light of sufficient energy, electron excitation from valence band to conduction band occurs. The holes left behind in the valence band then interacts with adsorbed water to form OH radicals. Although OH radicals are produced in-situ in both of these AOPs, the nature of pollutant and its interaction with the bubble or photocatalyst surface is crucial for their oxidation by OH radicals. This means that the OH radical utilisation for desired reactions is process specific. Nonetheless, the primary indicator of the process efficiency for comparing AOPs has often been the total OH concentrations. The characteristic high reactivity of OH radicals and a short life-span ($\sim 10^{-6}$ s) [13] makes it difficult to quantify them directly and also renders that the quantification of total OH radicals generated in-situ becomes highly unlikely.

To overcome the issue of direct quantification, a range of indirect methods have been developed, including; emission spectroscopy, laser induced fluorescence, electron spin resonance, spin trap and chemical probes [14–19]. Amongst the reported methods, chemical probes are a useful means of quantifying OH radicals due to their low-cost and relatively short analysis time. Several probes are frequently reported for OH quantification, namely; salicylic acid, terephthalic acid and coumarin. For instance, salicylic acid has been examined as a probe for the quantification of OH from PC [20], Fenton-based reactions [21] and cavitation [22,23]. Here the total OH radical concentration is determined as the sum of quantified hydroxylation products (2,3 dihydroxybenzoic acid, 2,5 dihydroxybenzoic acid and catechol) formed during the process. Similarly, Hirano & Kobayashi utilised coumarin to quantitatively detect OH radicals during AC, where the concentration of 7-hydroxycoumarin (7OHC) was directly related to the concentration of OH radicals [24].

Hydroxylated products formed as a result of the reaction between OH radicals and the probe molecules are monitored and related to the concentration of OH radicals based on stoichiometry. Furthermore, to calculate the total OH radicals, several approximations have been made. For instance, Zhang et al [25] estimated that 6.1 % of all OH radicals are scavenged as the fluorescent hydroxylation product (7OHC) when coumarin was used as the probe molecule. This approximation was attained from 7OHC yields obtained from γ -irradiation studies of coumarin and therefore may not be valid when translated to other AOPs. It is apparent that when using indirect methods of OH quantification such as probe based methods, the hydroxylated product yields are process specific. However, ignoring process conditions, hydroxylated product yields between methods have been translated to report total OH concentration. This renders the relation between hydroxylated product and total OH radicals as being inconsistent. In another example, when terephthalic acid was used as a probe to determine the total OH concentration produced during PC, an OH radical yield from laser photolysis of H_2O_2 was used to relate the concentration of hydroxylation product 2-hydroxyterephthalic acid to total OH radicals produced [26]. With the analytical quantification of total OH radicals being unlikely, this is the commonly utilised approach to determine total OH radicals and is rather misleading [25,27,28]. It is therefore important to establish process specific OH yields instead of reporting total OH radical concentrations as a means of comparing AOPs.

The aim of this study was to address this gap by employing coumarin as the probe molecule to quantify OH radicals produced by two different AOPs; AC and PC and compare their performances. Coumarin was selected as a probe due to its solubility in water, weakly luminescent state compared to its hydroxylated product (7OHC) and ease of quantification. The OH quantification procedure was established by initially proposing a pathway for the fate of OH radicals which was used to make deliberations, identify key yields and define relevant concentrations. The proposed procedure was then also used to assess previously reported coumarin based systems and address assumptions made therein to develop a method which can report a more meaningful process specific OH radical concentration.

2. Methodology

2.1 Materials

Coumarin and 4-Hydroxycoumarin were obtained from Acros organics, 3-Hydroxycoumarin, 3-(2-Hydroxyphenyl)propionic acid, and 7-hydroxycoumarin (7OHC) 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. Photocatalyst P25 TiO₂ was purchased from Evonik. Methanol (≥ 99.8 %) and acetic acid (≥ 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 hydroxycoumarins (20 μ M) were prepared to their desired concentration and diluted to operating concentrations with distilled water when required. A range of diluted solutions were prepared, and calibration curves of the standards were obtained using high performance liquid chromatography (HPLC). HPLC mobile phases were prepared using deionised water.

2.2 Experimental procedures

All experiments were carried out in 250 mL screw cap bottles, with 200 mL working volume of 100 μ M coumarin solution. 1.5 mL samples were taken at dedicated time intervals using a needle and syringe for analysis. Samples were then filtered with Millex syringe filters (pore diameter – 0.22 μ m) into HPLC vials for analysis. Treatment time for each process was 120 minutes. AC experiments were performed using a 500 W VCX 500 ultrasound probe (20 kHz) positioned inside the screw cap bottles with a tip depth of 1 cm (Figure 1 a). The tip of the ultrasound probe had a diameter of 13 mm and was operated at 90% amplitude. A separate 200 mL volume was prepared for each time point to avoid changes to tip dip height upon sampling. Experiments were performed in a cold water bath and sonicated in 20-minute intervals to maintain a solution temperature below 40 °C. PC experiments were performed with P25 TiO₂ photocatalyst loading of 0.1 g/L. A magnetic stirrer bar was placed inside each bottle which was positioned on a magnetic stirrer (operated at ~ 1000 rpm) and placed 4 cm in front of a UV-A/36 W Philips lamp (Figure 1 b and c). Prior to illumination, solutions were stirred in the dark for 40 minutes to ensure adsorption equilibrium between the photocatalyst and coumarin (minimum adsorption time determined according to 24-hour adsorption experiment, supplementary information Figure S1). PC experiments were initiated by switching on the lamp following dark adsorption period. A light control study was performed at the same conditions aforementioned, but in absence of TiO₂, to determine coumarin loss by UV light (photolysis).

Figure 1 - Schematic of experimental setups used for acoustic cavitation (a) and photocatalysis (b, top view and c, side view)

Sample analysis was performed using a HPLC. A Kinetex 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) gave the most effective separation between components. An additional 3 minutes run-time was added to flush the column in between runs. 5 μ L sample volume was injected into the column using an autosampler. The samples were analysed using an Agilent 1100 HPLC G1321A Fluorescence Detector (excitation wavelength: 332 nm, emission wavelength 450 nm) for 7OHC, and an Agilent 1100 HPLC G1365B Multi-Wavelength Detector (signal wavelength: 277 nm) for coumarin and all other compounds. Calibration curves were prepared for each compound to determine their relative concentrations during experiments.

3. OH radical generation and utilisation

The fate of OH radicals produced from AC and PC are given in Figure 2. OH radicals are formed at the surface of the catalyst (PC, Figure 2a) or the inner cavity (AC, Figure 2b) (as mentioned in section 1) and, in both cases, can diffuse to other regions [29,30]. These pathways are taken as the primary sources of OH radicals for each process and their complete quantification represents the total OH radical concentration ($[\text{OH}]_{\text{T}}$). Quantification of $[\text{OH}]_{\text{T}}$ is highly unlikely and for probe based quantification, it depends on the nature of the probe molecule and process conditions. Instead of trying to determine $[\text{OH}]_{\text{T}}$, various specific concentrations and yields can be defined and determined as a means of comparing AOPs. The three yields leading to $[\text{OH}]_{\text{T}}$ are α , β and δ . The significance of these yields as well as the feasibility to calculate them are discussed in this section.

Figure 2 indicates that a particular fraction of generated OH radicals ($\alpha[\text{OH}]_{\text{T}}$) react with the probe and the remaining fraction ($(1 - \alpha)[\text{OH}]_{\text{T}}$) will undergo alternative reactions (e.g. recombination) not involving the probe. $\alpha[\text{OH}]_{\text{T}}$ corresponds to the fraction of OH radicals utilised by the probe and can be represented as $[\text{OH}]_1$. The yield α can thus be defined by Equation (1). This yield represents the ratio of utilised OH radicals for hydroxylation to total produced OH radicals. However, the requirement of $[\text{OH}]_{\text{T}}$ to calculate this yield limits its use. Additionally, α is also dependent on the physico-chemical properties of the probe and its mode of interaction with the OH radicals.

$$\alpha = \frac{[\text{OH}]_1}{[\text{OH}]_{\text{T}}} \quad (1)$$

As the system in consideration is based on coumarin dosimetry, $[\text{D}]$ can be used to represent the mono-hydroxylated product 7OHC. Any hydroxycoumarin product can be chosen as $[\text{D}]$, however, since 7OHC can be distinctly identified fluorometrically and unambiguously, it was chosen as the main hydroxylated product. This allows for β to be defined according to Equation (2). This yield represents the fraction of $[\text{D}]$ formed from utilised OH radicals.

$$\beta = \frac{[\text{D}]}{[\text{OH}]_1} \quad (2)$$

Figure 1 – Schematic describing OH radical formation during a) photocatalysis and b) cavitation, and c) a suggested pathway and yields for OH radicals during reaction with a chemical probe. $[OH]_T$ – total OH radical concentration, $[OH]_1$ – concentration of utilised OH radicals, $[D]$ – concentration of detectable product, α – fraction of $[OH]_T$ reacting with probe molecule, β – fraction of $[OH]_1$ used towards detectable product $[D]$, and δ – fraction of $[OH]_T$ used towards detectable product $[D]$

The final yield, δ , represents the overall yield of $[D]$ produced from $[OH]_T$ generated. This is a convenient means to relate the concentration of a detectable product directly to that of total produced OH radicals in a process. Again, the need for a known $[OH]_T$, limits the use of this yield.

$$\delta = \frac{[D]}{[OH]_T} = \alpha \beta \quad (3)$$

As mentioned in section 1, chemical probes have been previously used to quantify total OH radicals on the following basis,

- (i) relating the concentration of $[D]$ to OH radical concentration stoichiometrically and
- (ii) applying a δ yield to calculate $[OH]_T$

The stoichiometric determination of OH radicals required to produce $[D]$ is valid, however there are inconsistencies surrounding δ due the ambiguous use of $[OH]_T$. Specifically, for coumarin based OH quantification methods, δ yield determined from γ -irradiation of coumarin have been used to calculate $[OH]_T$ for various AOPs. This method assumes δ is constant across AOPs and γ -irradiation.

Although this is unlikely, it is frequently reported [25,27,28]. Our group had also reported results based on these assumptions, however, revisiting the OH radical quantification pathway enabled us to devise the proposed methodology.

Zhang et al [25] utilised radiation chemical yields (no. of molecules/100eV) from two γ -irradiation studies to determine δ yield for γ -irradiation Equation (4) and applied this to their PC study. This resulted in an approximation that 6.1 % of all OH radicals are scavenged as 7OHC in coumarin solutions. Although this may be true for γ -irradiation it may not be the case for other AOPs.

$$Total\ OH\ yield = \delta = \frac{G_{7OHC}(nmol/J)}{G_{OH}(nmol/J)} = 0.061 \quad (4)$$

Applying the same δ yield across AOPs assumes it to be constant regardless of the system and process conditions involved. However, when the proposed OH system is considered it can be seen that for δ to be constant across processes, both α and β must also be constant. Although it may be feasible for β to remain constant, given that it represents the yield of a common reaction across all processes, it is unlikely α will also be constant across different AOPs. α depends on the contact pattern between OH and the probe molecule, which tends to vary across AOPs according to their methods of OH generation and even within AOPs due to difference in process conditions. For example, P25 TiO₂, a UV activated photocatalyst, forms OH radicals from water and due to its higher coumarin adsorption capability might produce more 7OHC when compared to WO₃, a visible light activated photocatalyst with limited coumarin adsorption and whose OH radical generation is predominantly via the superoxide radical route [28]. For the two AOPs considered in this work (PC and AC) it has been demonstrated that each of their regions (Figure 2) attribute to the overall decomposition of a probe molecule to varying degrees [29–31] according to its physico-chemical properties. The very different nature in location of OH radical generation and their contact with the probe molecule in different AOPs, make it highly unlikely that the extent of utilisation (α) remains constant across AOPs despite using the same probe molecule. Therefore, utilising δ -yields from other processes does not provide authentic total concentrations of OH radicals as presented in literature thus far.

δ -yield may become a viable means for reporting $[OH]_T$, when $[OH]_1$ tends to $[OH]_T$. This has been achieved with γ -irradiation studies of sodium formate. The technique for quantification of radical species in γ -irradiation has been established as; selecting appropriate solvent, measuring chemical change, and assume reaction sequence to relate chemical change to the desired radical species [32].

For the sodium formate and oxygen (Equations 5 and 6) system, the chemical radiation yield of OH (G_{OH}) was determined by relating the concentration of CO_2 with the concentration of OH.

This procedure equates $[OH]_1$ to $[OH]_T$ by monitoring the detectable product $[D]$. This was achieved by selecting appropriate operating conditions (e.g. sufficient O_2 concentrations) to minimise undesirable side reactions, ensuring the concentration of scavenger ($HCOO^-$) was sufficiently high to scavenge OH radicals, and accounting for (spur) scavenging using the appropriate correction factors [32,33]. Applying these measures essentially equates α to 1 in Equation (1) and allows for the assumption that $[OH]_T = [OH]_1$. This is further validated by numerous γ -irradiation studies [33–36] reporting radiation chemical yields with a good agreement of OH radiation yield at neutral pH as 2.7 (± 0.07) molecules/100 eV. Therefore, it is feasible to calculate $[OH]_T$ to determine δ for γ -irradiation processes.

No studies have however been performed into the total radical yields of AC and PC processes making it impossible to determine the total amount of OH radicals in a similar manner. Furthermore, both processes represent non-homogeneous systems (Figure 2) which presents additional difficulties for quantification studies. The dependency of α on the physico-chemical properties of the probe as well as location of radical generation and nature of their contact with the probe molecules is a significant restriction when investigating radical yields. For example, Leandri et al [37] investigated the application of coumarin as a quantitative probe during PC and found its low solubility restricts complete surface saturation of the catalyst, making quantification of total OH radicals impossible. Additionally, Zupanc et al [23] attempted to quantify OH radicals during hydrodynamic cavitation and demonstrated higher concentrations of the probe molecule (salicylic acid) influences the fluid properties, which affects the degree of cavitation (and OH radical mediated reactions). These difficulties present a degree of uncertainty when reporting $[OH]_T$ with such probes.

The difficulty in determining $[OH]_T$ may shift the focus from utilising δ to β . As both $[D]$ and $[OH]_1$ are relatively simple to determine in a process and β is a convenient means of determining probe reacted ($[P]$). However, it is highly likely that β may remain constant across AOPs and also be dependent on $[D]$ which is subject to degradation [38,39]. Additionally, the degree of degradation of $[D]$ will be dependent on the operating conditions and nature of the process which may result in a lack of

constancy when translating across AOPs. To avoid the same uncertainties as experienced with δ , simply reporting $[\text{OH}]_1$ alongside operating conditions may be a more convenient method to compare AOPs. This can still provide insight to OH radical production in AOPs by providing a relative means of OH comparison [39] in addition to identifying most effective conditions for OH radical production/utilisation for that probe. Based on the proposed OH pathway and previous attempts at probe based OH quantification, it is suggested that reporting $[\text{OH}]_1$ or $[\text{P}]$ is a more suitable method of reporting OH radical concentrations and assessing AOPs rather than $[\text{OH}]_T$.

4. Results and discussion

4.1 Coumarin hydroxylation during photocatalysis and cavitation

The measured concentration profiles of coumarin and 7OHC during a two-hour PC experiment are shown in Figure 3. The initial concentration of coumarin, C_0 was 100 μM and P25 TiO_2 catalyst loading was 0.1 g/L, irradiation began following dark adsorption equilibrium (~6 % coumarin adsorption). Coumarin was rapidly consumed within the first 20 minutes of irradiation, with a gradual slowing and near complete removal at 120 minutes. 7OHC was formed immediately up to a maximum concentration of 6 μM at 20 minutes, after this a steady decrease until its complete removal at 120 minutes was observed. The observed trend is typical of coumarin and 7OHC profiles reported in PC systems [25,27,28] and highlights the effective performance of P25 TiO_2 as a highly oxidising photocatalyst. The performance may be attributed to its adsorption affinity towards coumarin, which facilitates reactions with surface-bound OH radicals.

The formation of 7OHC and other hydroxylated products confirms the production of OH radicals in the process. Monitoring 7OHC concentration enables indirect OH quantification as previously suggested [22]. However, 7OHC is also prone to oxidation and will compete for OH radicals as shown in previous studies [38,39]. Confirming this, it can be clearly seen in Figure 3 that the concentration of 7OHC increases in the initial stages of the experiment followed by an eventual decrease (concentration profiles of additional products available in Figure S2 of supplementary information). When coumarin is present in excess during the initial stages of the reaction (highlighted as the inset of Figure 3), linear coumarin removal was observed attributing it to zero order kinetics. The competition for OH radicals by 7OHC and other hydroxylated products resulted in slower reaction rates of OH radicals with coumarin and also deviates from a zero-order reaction beyond the initial 5 minutes. At much higher initial concentrations of coumarin, zero order exhaustion of coumarin would be observed at a longer

time period [27]. Recently, Ollis reported that the initial rate of the reaction during photocatalysis truly represents the intrinsic reaction order (zero order) whereas the whole data set might be disguised as a first order reaction [40]. The zero order PC reactions reported as first order reactions are predominantly due to the intermediates that are formed during the course of PC oxidation which interfere with the light absorption or catalyst surface saturation. In typical degradation studies using PC, since the aim would be to mineralise the parent compound, much attention is usually not diverted towards intermediate product kinetics. Hence, the first order rate constant is reported by only tracking the parent compound's concentration. Whereas, to assess the performance of PC using a probe such as coumarin, it is required to monitor the kinetics of its intermediates/hydroxylation products. This explicitly highlights that it is the intermediates that shift the reaction order of the parent compound from zero to one. Therefore, with the OH radical generation being constant for the given process conditions, the OH radical consumption rate must also be constant and can be calculated based on the zero order constant obtained for $t = 0 - 5$ min.

Figure 3 – Concentration profiles of coumarin (C/C_0) and 7OHC during PC; $t=0-120$ minutes (Inset graph give profiles for $t=0-5$ minutes), $C_0 = 100 \mu\text{M}$, P25 TiO_2 loading – 0.1 g/L

Figure 4 shows the coumarin removal and 7OHC formation profile during cavitation treatment carried out with the same initial concentration as that of the PC experiments ($C_0 = 100 \mu\text{M}$). After 120 mins of sonication, ~20 % of coumarin was consumed and almost $3 \mu\text{M}$ of 7OHC had formed, indicating a much

lower concentration and rate of OH formation compared to PC and exhibiting zero-order kinetics throughout the process (concentration profiles of additional products available in Figure S3 of supplementary information). The lower coumarin removal with AC may be attributed to the chemical nature of the coumarin probe and its interaction with cavities. Each region of a cavity provides a different degradation pathway [29], either pyrolysis (inside the cavity) or hydroxylation and ring opening (gas-liquid interface/bulk) and contribute to the overall probe conversion to varying degrees. It has been shown that the physico-chemical properties of a pollutant (vapour pressure, pK_a and $\log P_{\text{oct/wat}}$) [29,41] influence which degradation pathway is most dominant due to the location of the pollutant with respect to each region. The physico-chemical properties of coumarin indicate that the main pathway of degradation during AC will be hydroxylation in the bulk and interface but not pyrolytic effects. This is due to the low vapour pressure making evaporation into the cavity unlikely, and the combination of coumarin's inability to donate a proton and moderate hydrophilicity ($\log P_{\text{oct/wat}} = 1.39$) restricting its location to the bulk region. Coumarin mainly in the bulk limits its contact with OH radicals due to their short life spans, which imply that diffusion of OH into the bulk to carry out oxidation reactions is mass transfer limited. Times scales of OH diffusion to bulk have to be smaller than its half-life to capture most of the generated radicals with minimal loss to undesirable reactions. Therefore, coumarin is less likely to come in contact with OH radicals in the bulk region than the gas-liquid interface and thus results in a relatively lower overall removal.

Figure 4 – Concentration profiles of coumarin (C/C_0) and 7OHC during AC treatment $t=0$ –120 min, C_0 - 100 μM

4.2 Determination of $[\text{OH}]_1$

As described earlier in section 3, when using chemical probes, it is only possible to determine $[\text{OH}]_1$ but not $[\text{OH}]_T$ when assessing AOPs. Although it has been suggested that coumarin is more useful as a qualitative probe for OH radicals [42], it may be employed quantitatively to determine $[\text{OH}]_1$ with the appropriate deliberations. It is first established that coumarin reacts to form a variety of hydroxylation products upon contact with OH [43]. These reactions occur by the addition of an OH radical to the coumarin molecule, forming a radical adduct which further reacts to generate the hydroxylated coumarin products [43]. The overall reaction occurs in 1:1 stoichiometric ratio between coumarin and OH radicals, so that the concentrations of these products are directly related to $[\text{OH}]_1$ (i.e., 1 mole Coumarin + 1 mole OH radical $\rightarrow$ 1 mole mono-hydroxylated product). However, it is also possible for coumarin to undergo reactions with different stoichiometric ratios, such as di-hydroxylation. These are only considered significant during higher levels of coumarin conversion where the likelihood of mono-hydroxylated product interacting with OH radicals is higher. This is supported by the reaction mechanism suggested by Milenkovic et al [44] who demonstrate di-hydroxycoumarin formation from mono-hydroxycoumarins. As such, subsequent calculations with $[\text{OH}]_1$ were only performed during low conversion regions.

It is also possible to determine $[\text{OH}]_1$ through the quantification of total hydroxylation products. However, during both processes, it was observed that there remained a significant difference between total hydroxylation product concentrations and $[\text{P}]$. During the zero-order conditions the yields of hydroxylation products from $[\text{P}]$ were calculated as $21 \pm 5 \%$ and $33 \pm 7 \%$ for PC and AC respectively (relative hydroxylation product distribution available in T1 of supplementary information). The low yield of hydroxylation products in both cases may be attributed to OH mediated reactions favouring ring opening mechanisms [43] instead of hydroxylation, or the subsequent degradation of generated hydroxylation products.

To determine $[\text{P}]$ accurately, it is also important to consider pathways where coumarin may be consumed in the absence of OH radicals. In PC systems, this can be via UV light photolysis, adsorption and other radical species. To account for photolysis, light control experiments were performed where the coumarin solution was irradiated without catalyst to determine the rate ($\sim 0.2 \mu\text{M min}^{-1}$) at which coumarin was consumed via photolysis (Figure 5). The resultant chromatograms obtained from samples did not show the formation of hydroxylated products. This indicated that the removal of coumarin is not a result of hydroxylation under photolysis, and coumarin removed via this path was accounted for in each time point according to Equation (7). This corresponded to $[\text{OH}]_1$ for PC experiments. Coumarin may also interact with different radical species (such as superoxide radical [45]) but the degree to which these react with coumarin remains unclear. Although it is agreed hydroxycoumarins are a result of OH-coumarin interactions, it is also possible for fragmentation products to form via OH radicals [43]. As it is unclear to what extent OH-mediated fragmented products are formed compared to different radicals, Equation (7) was tentatively used to represent $[\text{OH}]_1$ with the acknowledgement that it may be modified to account for coumarin loss due to non-OH radical attack.

For AC systems, the pyrolytic effects can be considered negligible with coumarin and degradation is likely to only occur via hydroxylation in the bulk liquid. This means any coumarin consumed during AC treatment was attributed to reaction via OH radicals [Equation (8)] and $[\text{P}]$ was assumed the same as $[\text{OH}]_1$. Hydrogen radicals are also generated during AC processes and may offer another degradation pathway, either directly or indirectly. However, as their reactivity with coumarin is largely unknown a similar approach is taken here as with PC, where any loss via hydrogen radicals is negated. However, it is acknowledged that Equation (8) could be modified to account for this.

$$[OH]_{1,PC} = [Cou]_{reacted,PC} = [Cou]_{consumed,PC} - [Cou]_{UV} \quad (7)$$

$$[OH]_{1,AC} = [Cou]_{reacted,AC} = [Cou]_{consumed,AC} \quad (8)$$

where, $[Cou]_{reacted}$ is the concentration of coumarin reacted, $[Cou]_{consumed}$ is the total amount of coumarin removed, $[Cou]_{UV}$ is the concentration of coumarin removed via photolysis and subscripts PC and AC indicate the corresponding concentrations for photocatalytic and acoustic cavitation systems, respectively. Using Equations (7) and (8), the concentrations of utilised OH radicals were calculated for AC and PC based on measured values of $[Cou]_{reacted}$.

Figure 5 – Coumarin removal via photolysis (UV only), t=0–120 min, C_0 - 100μM

4.3 Determination of β -yield

Monitoring the hydroxylated products indicate that the removal of probe molecule is due to the hydroxylation reactions and not due to other undesirable reactions. As mentioned, the hydroxylated product 7OHC was taken as [D] and used for further calculations. The corresponding β -yields for both the AOPs were then determined for zero-order conditions to reflect the expected linear production rate of OH. Once determined for each time point, they were plotted against concentration of coumarin reacted to determine if it is constant as the reaction proceeds. Figure 6 indicates that the β -yields

decreases as C/C_0 decreases for both processes. The trends for β can be better understood by revisiting its expression in Equation (2), where it is defined as the ratio of 7OHC to coumarin reacted. The quantity of coumarin reacted is dependent on its proximity to OH radicals during a particular AOP, as expressed by α . However, 7OHC is also subject to OH radical oxidation and other possible degradation pathways. Therefore, [7OHC] at a particular time is a result of its generation and consumption as expressed in Equation (9). The amount of 7OHC generated is only dependent on the amount of coumarin reacted but its consumption will vary according to the selected process and its operating conditions.

$$[7OHC] = [7OHC]_{generated} - [7OHC]_{consumed} \quad (9)$$

The gradual decrease observed with β can be attributed to the increasing concentration of 7OHC in the system increasing its likelihood of reacting via one of the potential degradation pathways available. The larger error bars in the β profile during PC may be a result of the experimental procedure selected to perform experiments. In this set-up (Figure 1 b and c), the centre bottle may receive a greater degree of light intensity compared to those on the outside. An increased light intensity leads to an increase in PC activity [46]. When an average yield was taken of all the values for each process, it was found that AC and PC gave β of $15 \pm 2 \%$ and $18 \pm 4 \%$, respectively.

The observed β values can be explained by Equation (9). This indicates a lower β is due to a greater amount of 7OHC consumption during a process. To further analyse the yields of AC and PC the zero-order degradation rate constants of coumarin and 7OHC were determined for each process (degradation profiles available in Figure S4 of supplementary information). 7OHC degradation was not observed during AC treatment, therefore Individual samples of 7OHC at comparable concentrations ($5 \mu\text{M}$) were sonicated to determine its rate constant during AC. The zero-order rate constants were calculated for dimensionless 7OHC profiles during $t = 40 - 120$ min for PC and $t = 0 - 60$ min for AC and are summarised table 1. The larger rate constant for 7OHC during AC is likely due to the difference in physico-chemical properties which determine proximity to cavities. As both molecules have a comparable vapour pressure, their performance is likely due to differences in pK_a and $\log P_{\text{oct/wat}}$ values.

It was also observed that coumarin has a higher rate constant than 7OHC during PC. This may also be explained by considering the molecular states of the two compounds and the point of zero charge (zpc) of the TiO_2 catalyst. The zpc of TiO_2 is known to exist between pH 6 – 7 [47], at which point it will have no overall charge and its surface will be dominated by neutral species. As coumarin was entirely

in its neutral molecular state and 7OHC only partially (pK_a values determined using MarvinSketch software), it was more likely for coumarin to interact with surface-based OH radicals and hence resulted in a greater rate of removal.

Process	$k_{\text{cou}} (\times 10^{-4})$	$k_{7\text{OHC}} (\times 10^{-4})$
AC	16 ± 2	130
PC	420 ± 35	120 ± 1.5

Table 1 – Apparent zero-order removal rate constants ($\mu\text{M min}^{-1}$) of coumarin and 7OHC (denoted k_{cou} and $k_{7\text{OHC}}$, respectively) calculated for AC and PC treatment. Standard deviations are shown based on replicate experiments except for $k_{7\text{OHC}}$, AC where a single experiment was performed

Figure 6 also shows β -yields calculated from previously reported studies where the same AOPs were used with coumarin aqueous solutions. Values from literature were calculated during zero-order conditions. Each data set shows a clear variation across processes, though all have a trend of gradual decrease. When considering PC processes, the lower values observed with Nagarajan et al [28] and Buck et al [27] may be explained by considering the type of lamp used to irradiate the photocatalyst and its intensity. The UV bulb used by the authors had a shorter emission wavelength than that used in this study. Shorter wavelengths have been shown to improve catalyst performance in terms of quantum yields [48] and could also cause a greater degree of 7OHC consumption resulting in a lower β -yield. Additionally, the distance between the lamp and the reactors were not the same (4 cm reported here compared to 11 cm for Nagarajan et al/Buck et al) which would also affect light intensity which is square of the illumination distance and accordingly, the greater distance between the lamp and the reactor in the case of Nagarajan et al and Buck et al's work would have impacted the OH radical production.

Similarly, from Kobayashi & Hirano's report, a lower β was calculated as compared to the value reported here for AC. This difference can be attributed to the types of sonication devices utilised during treatment. The data reported for β during AC was obtained using a 20 kHz ultrasound horn, whereas the β -yield calculated for Kobayashi and Hirano [24] was found using a 500 kHz ultrasound bath. The performance of these two methods of AC has been assessed previously [49], where the US bath shows greater performance in pollutant degradation due to a wider energy dissipation area resulting in larger amount of cavity generation. The increased degradation performance can also cause a greater removal of 7OHC compared to acoustic horn systems that results in a lower β value.

The variation in β across processes (Figure 6) indicate that its application is dependent on particular operating conditions of a process and cannot be applied outside of these without being re-calculated for new conditions (for example, comparison of β values reported by Nagarajan et al 2017 and Buck et al 2018). This indicates that, a single representative yield (β) is not possible for a process. This is due to the complex relationship between physico-chemical properties of a probe, selected operating conditions and regions of OH radical availability in an AOP, which determine the extent of OH utilisation. As each of these conditions (if not processes) will undoubtedly vary across studies, $[\text{OH}]_1$ (coumarin reacted) may be a more useful means for comparing AOPs. Hence, it is reiterated that comparisons between AOPs based on OH radicals should be restricted to concentrations of $[\text{OH}]_1$ alongside their chosen operating conditions.

Figure 6 – β vs C/C_0 for acoustic cavitation and photocatalysis processes, C_0 – 100 μM , catalyst loading - 0.1 g/L, closed symbols indicate values calculated from literature, open symbols indicate values collected in the present study

4.4 Comparison of AOPs

As the focus of the study is restricted to OH radical quantification, the following comparison is based only on the concentration of $[\text{OH}]_1$ without accounting for process energy consumption. To compare the processes, the zero-order rate constants were calculated for the $[\text{OH}]_1$ profiles. As seen in Figures 3 & 4, it is evident that OH radicals are utilised at a greater rate during PC than AC. Their OH utilisation rates were determined to be $4 \mu\text{M min}^{-1}$ and $0.16 \mu\text{M min}^{-1}$ respectively. The difference in utilisation is attributed to a greater compatibility between the physico-chemical properties of coumarin and the nature of the PC process. It is important to note that such rates are a function of the selected operating conditions. As the operating conditions are an important factor in total OH radical production for each process, these will also affect the rate at which OH radicals are utilised. Therefore, when considering any values representative of an AOP, the conditions at which they were obtained must be carefully considered.

Previous yields [25] reported for coumarin based quantification studies represent a convenient method for relating 7OHC to OH radicals, however this method requires the assumption of a constant utilised fraction (α) of OH radicals. As this was shown to be unlikely for AC and PC, employing this yield results in inaccurate reporting of total OH radical concentrations. It is suggested to instead report utilised OH radical concentrations as these are more representative of a process and its operating conditions. Employing this procedure allows for comparisons to be made across AOP and acknowledging limitations of the interactions between the probe and catalyst/bubble allows for proper interpretation of the resulting data.

5. Conclusion

Coumarin was employed as a probe to quantify OH radicals during both AC and PC processes and compare their performance. Firstly, a pathway for OH radical utilisation was proposed for both AOPs by defining relevant yields. Then it was determined that total OH radical concentrations reported in literature based on constant δ -yields from γ -radiolysis (and translating it across AOPs) are misleading. Therefore, it was suggested that analytical determination of total OH radical production is highly unlikely and instead, OH radicals utilised (or the concentration of probe molecule hydroxylated) must be reported as a means for comparing AOPs. To report the OH radicals utilised, the concentration of coumarin reacted was calculated by negating the coumarin loss observed due to non-OH radical mediated pathways. Their zero order OH utilisation rate constants were determined to be $4 \mu\text{M min}^{-1}$

¹ for PC and 0.16 $\mu\text{M min}^{-1}$ for AC. The difference in rates were discussed based on the fate of OH radicals and the nature of the reactivity of the probe molecule. Hence it was concluded that the most effective way to use probes for OH quantification is to determine utilised OH radical concentrations, while making the appropriate considerations for undesirable degradation pathways. Employing this methodology ensures more accurate means for comparing AOPs while acknowledging the limitations of such probe-based techniques.

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