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The development and optimisation of an immobilised photocatalytic system within a Stacked Frame Photo Reactor (SFPR) using light distribution and fluid mixing simulation coupled with experimental validation

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Abstract

Recently, photocatalytic reactors have been designed with a view towards overcoming mass transfer limitations especially in systems with immobilised catalysts. This paper reports the design of a titanium “bladed” propeller with TiO₂ immobilised on the blades. To evaluate the propeller efficiency, modelling using COMSOL Multiphysics® was validated experimentally using coumarin as a probe molecule allowing for OH radical quantification. Modelling of light distribution and catalyst irradiance at varying irradiation distance was performed using ray optics, which, alongside experimental work, showed that irradiation at 4 and 5 cm from the propeller yielded the highest irradiance (29.3 and 22.1 mW/cm²) and OH radical concentrations (5.38 and 5.56 µM respectively). Propeller rotation was modelled and compared against experimental data to assess mass transfer limitations at varying rotation speeds. This showed that 300 RPM provided the highest rate of coumarin degradation (0.32 µM/min) despite the model showing higher fluid velocities at 400 RPM.

1. Introduction

Over the last 40 years, research and development into photocatalytic technology has grown significantly, with the range of applications of photocatalysis becoming increasingly diverse [1]–[10]. The initial photocatalytic study carried out by Fujishima and Honda in 1972 [1], precipitated significant interest in water splitting, with many publications in recent years [2], [3]. Studies on environmental remediation for water and air treatment [4]–[7], microbe destruction [8], CO₂ reduction [9] and bioenergy production [10] have also been reported. As a result, several photocatalytic materials have been developed to increase photocatalytic efficiency, stability, visible light activation and selectivity. Despite these advancements in material design, reactor engineering has not advanced at the same rate.

Most chemical engineering reactors are well established but in photocatalysis there is still scope for novel designs, with light delivery being a unique parameter resulting in alterations to recognised reactors in industry. Effective irradiation, catalyst deployment and minimisation of mass transfer limitations are also key challenges in photocatalysis which have impacted on the scale up of photocatalytic reactors. Catalyst deployment is a crucial parameter in any design and is typically used to classify photo reactors into two groups, suspended or immobilised catalyst systems. Suspended reactors such as the Taylor vortex reactor [11], falling film reactor [12] and the propeller fluidised photo reactor (PFPR) [13] have been already proposed for formate degradation, salicylic acid degradation and hydrogen production respectively. One drawback of suspended systems is that downstream separation of the catalyst is required, which can add significant cost to the overall process, hence why there has been significant focus on development of robust, immobilised photocatalytic systems. Reactors such as the optical fibre photo reactor (OFPR) [14] and the rotating disk reactor proposed by Dionysiou *et al.* [15] for the treatment of organic pollutants in water, use an immobilised TiO₂ catalyst. A more recent example of an immobilised system is the static Kenics® mixer reported by Diez *et al.* [16], where the authors describe intense fluid mixing under laminar flow conditions around a coated catalyst surface.

Despite recent interest in reactor design, photocatalysis still requires the development of novel photo reactors which are adaptable and scalable, with capability of being utilised for a multitude of applications [17]. One such reactor is the stacked frame photocatalytic reactor (SFPR) proposed by Nagarajan *et al.* who carried out the modelling of mixing regimes and cellulose particle tracing [18]. As part of reactor design and subsequent manufacture, simulation and modelling has been demonstrated to provide valuable insights into reactor operation and optimisation [12], [19], and hence aid the reactor development process. Nevertheless, modelling can only provide an indication on how efficient a new photocatalytic process may be and information surrounding the chemistry of a reaction, especially regarding kinetics can only be provided by experimental validation. This was a key point stressed by Li Puma and Yue [20], where they showed the importance of combining modelling with experimental validation through use of an efficient screening process.

A variety of compounds have been used to quantify the efficiency and performance of photocatalytic systems. Chemicals such as methylene blue [21] and organic pollutants such as 4 – chlorophenol [14], [22] have been reported for analysis of photocatalytic

activity. Terephthalic acid is also capable of providing an indication of the number of photogenerated OH radicals [23]. OH radical generation is crucial in a number of photocatalytic environmental remediation processes, where the radical is the primary oxidising agent driving bacterial disinfection and wastewater treatment. More recently, coumarin has emerged in literature as a photocatalytic probe molecule [24]–[26] that can be used to monitor OH radical generation by analysing coumarin conversion to 7 – hydroxycoumarin.

This paper reports the development of an immobilised photocatalytic system, which employs a novel SFPR design where TiO₂ (anatase) was annealed onto a titanium propeller. As part of the development process, COMSOL Multiphysics® has been used to model the distribution of UV light through the reactor with focus upon the link between reactor geometry and characteristics of the light source used, as well as irradiance on the catalyst surface at varying irradiation distances. Furthermore, the rotation speed of the propeller and subsequent fluid velocity and mixing patterns have been modelled to help understand mass transport limitations, and how these can be minimised. Particular attention has been given to the experimental validation, where the modelling results have been compared against the observed coumarin degradation at predefined irradiation distances and rotation speeds, which provides kinetic information unknown by the model.

2. Experimental

2.1 Reactor Concept

The photocatalytic reactor was based on a plate and frame design. Perspex frames (thickness 10 mm) were modified to allow the placement of a titanium (Impact Ireland) “blade” (Figure 1) which acts as a photocatalytic propeller. Propeller rotation promotes fluid mixing to help overcome mass transport limitations. The design is adaptable, allowing for change of material and design parameters in the future e.g. the number of catalyst coated blades. The titanium propeller was coated with TiO_2 made using the Sol-gel process as described by Mills *et al.* [27], with a manual dip coating method being employed. The propeller has a coated surface area of 16.34 cm^2 . A UV-A LED (LED Engin) with a peak wavelength of 365 nm was used to irradiate the TiO_2 catalyst.

Figure 1; (a) Schematic of the SFPR with the rotating titanium propeller housed within the reactor. (b) Image of the reactor under UV irradiation (c) Dimensions of the propeller within a frame of the SFPR (d) Cross-sectional diagram of the titanium propeller. (all dimensions in mm).

2.2 Finite element modelling

A number of key parameters were considered during the modelling process and are shown below in Table 1;

Geometrical ray optics	
n	Refractive index (real part)
k	Refractive index (imaginary part)
λ	Wavelength (nm)
I_{th}	Threshold intensity of reflected rays (W/m ²)
γ_s	Probability of specular reflection
α	Absorption coefficient (fraction of light absorbed)
r	Smoothing radius (m)
N_w	Number of rays in wave vector space
P_{src}	Total source power (W)
I	Irradiance (mW/cm ²)
Turbulent Flow k - ϵ (Fluid mixing)	
P_{ref}	Reference pressure (Pa)
T_{ref}	Reference temperature (K)
ρ	Fluid density (kg/ m ³)
μ	Dynamic viscosity (Pa·s)
f	Revolutions per time (1/s)

Table 1; Parameters that have been considered in the modelling process.

2.2.1 Ray Optics

The geometrical ray optics module within COMSOL Multiphysics® 5.3a uses a graphical interface to trace the distribution and trajectory of rays through a geometrically defined system as shown recently by Roegiers *et al.* [28], where a detailed theory about the method can be found. The characteristics of a photocatalytic light source can be specified, and in this case based upon the UV LED used in photocatalytic validation experiments. The SFPR geometry was defined, including the Pyrex end plates and the titanium propeller, which was then coupled with the required physics and meshing, where the 70° viewing angle and conical distribution of the light source used was input using the release from grid function. The total source power was experimentally obtained as 0.526 W by using a neutral density filter (Balzers) and a UV-X radiometer to analyse the irradiance at the source of the LED, measured at 5 mW/cm². The neutral density filter allows only 0.95 % of light through, meaning the total irradiance at the source was 526 mW/cm² and since the UV-X radiometer has a sensor of 1 cm² the total source power could be evaluated. The power carried by each ray in the model is a function of the total power divided by the number of rays emitted from the source. A physics controlled normal mesh was used (Figure 2 (a)).

Two separate models were completed, with the first analysing the ray trajectories through the reactor. This model used a sample number of 100 rays (N_w) for visual clarity and the second model used 10^5 rays as a more realistic representation of a LED light source. The purpose of the second model was to evaluate the attenuation of UV-A light to the TiO_2 catalyst surface based upon a predefined absorption coefficient. The average irradiation (mW/cm^2) on the face of one of the illuminated blades was evaluated in COMSOL using a surface integral.

2.2.2 Computational fluid dynamics

COMSOL Multiphysics® 5.3a was used to model the fluid velocity profile within the SFPR upon a uniform rotation of the titanium propeller. In particular, the velocity profiles of fluid surrounding the catalyst surface were determined. The modelling was done through use of the *rotating machinery turbulent flow k - ϵ* model, with the geometry of the reactor being changed from that used in the ray optics model. For this part of the modelling only the reactor chamber was defined in the geometry with the removal of the glass plates and the addition of a rotating domain as shown in Figure 2(b). Water was used as the fluid and values for density ($1000 \text{ kg}/\text{m}^3$) and dynamic viscosity ($1.002 \times 10^{-3} \text{ Pa}\cdot\text{s}$) were input.

The rotating domain was assigned (0.025 m), and the general revolutions per time, f , which was used to dictate the rotation speed of the blades (RPM) about the x-axis, was controlled using the global parameter ω . A normal mesh was used (Figure 2 (b)) to provide a higher degree of accuracy than a coarse mesh with small variation (<6 %) between meshes. Once the mesh was created a parametric sweep was then initialised in COMSOL to vary the values of the parameter ω for the closed system. A frozen rotor study was combined with a time dependent study for each value of ω used in the model. The final time step of 1 s was used for analysis when the model was assumed to be in a steady state condition.

Figure 2; Meshing of the reactor and propeller for (a) geometrical ray optics, including both Pyrex end plates (b) CFD modelling of the fluid mixing patterns where, only the inner reactor chamber is modelled.

2.3 Photocatalytic procedure

In a typical experiment, 48 mL of coumarin solution of concentration 100 μM was made up in a beaker and injected into the SFPR via a sample port. For irradiation distance optimisation a constant rotation speed of 10 RPM was employed and for rotation speed optimisation an irradiation distance of 5 cm was used. The propeller was coupled to a bilge pump (Seaflo) which was used to control the speed by varying the voltage applied, and an oscilloscope (Tektronix, TD 2022B) was used to determine the correlation between voltage and rotation speed for the bilge pump. Samples were taken every 15 min for analysis over a 2-hour period. A sample volume of 1.5 mL was injected into a Quartz cuvette and analysed in a Cary 300 UV/Vis spectrophotometer, which was used to monitor the absorbance of coumarin at a wavelength of 277 nm with a scan rate of 200 nm/min. The absorbance was compared to a calibration graph of known concentrations.

A sample volume of 3.5 mL was injected in to a standard plastic cuvette and placed in a Perkin Elmer LS 50B Luminescence Spectrometer Fluorimeter to monitor the concentration of 7-hydroxycoumarin, which has an excitation peak at 332 nm and an emission peak at ~ 450 nm. The intensity of the emission at 450 nm was recorded and compared against a calibration graph of known concentrations and used as an indication of the concentration of OH radicals formed during the reaction. According to literature 6.1 % of the products formed from coumarin breakdown is predicted to be 7-hydroxycoumarin [25], [29], [30], therefore using this ratio, the total number of OH radicals generated can be evaluated.

Actinometry was carried out to determine the photon flux and photonic efficiency of the LED light source and carried out using the potassium ferrioxalate actinometrical method [31], [32]. As the propeller is in a central position within the reactor, light must first travel through coumarin solution to reach the catalyst surface. Therefore, rather than replacing the entire solution with ferrioxalate, the actinometry solution was only placed in the two frames which house the propeller (24 mL) and a further frame was added between the LED and the actinometry solution, with these two solutions being separated via an additional Pyrex plate. The extra frame was filled with 100 μM coumarin solution to best simulate the conditions through which light must travel. A diagram of this setup is shown below in

Figure 3.

Figure 3; Schematic representation of the setup used for actinometry experiments

3. Results and Discussion

3.1 Ray optics and irradiance modelling

While the relationship between irradiation source and catalyst surface is paramount to any photocatalytic system, it can often be overlooked in the literature with more focus on simply achieving high irradiance. The irradiance on a target surface, however, is a key parameter and one that should be investigated to improve the design and development of more efficient photocatalytic reactors. Two key features, which determine the catalytic activity of the system, are the delivery of photons and subsequently the irradiance on the catalyst surface. To investigate these parameters further, COMSOL simulations have been run to model both ray trajectories and irradiance on the surface of a catalyst coated propeller. Both were modelled as a function of the distance between a UV-LED and the propeller.

To date, there has been fewer than ten publications using COMSOL to evaluate the ray optics of a photocatalytic system. In a recent paper, Roegiers *et al.* used COMSOL to plot ray trajectories for a multi-tubular gas phase reactor, using a thin dielectric film to model the TiO_2 sol-gel present on the surface of the tubes [28]. The imaginary part of a refractive index, k , was used to describe the light absorption for this TiO_2 thin dielectric film. In this work for a liquid phase reactor, an alternate approach was taken, and a boundary condition of mixed diffuse scattering and specular reflection was allocated to the titanium propeller. The absorption coefficient (ranging from 0 – 1), α , was input and the irradiance on the catalyst surface was calculated based upon the predefined value, $\alpha = 0.7$, for thick titania films as reported by Mills *et al.* [33]. The model has also included the refractive indexes of Pyrex (1.474) and water (1.333). Ray trajectories and irradiance computations were assessed at two distinct angles of blade rotation, namely at the initial position (Figure 4 (a)) and after a 45° rotation (Figure 4 (b)).

Figure 4; Initial ray trajectories directed towards the SFPR before collision, showing the point source and conical distribution. Shown here is the two configurations of the propeller used for ray tracing evaluations.

Modelling the light source can indicate the optimum distance and type of light distribution to allow the maximum number of rays possible to enter the reactor, thereby enhancing the irradiance at the photocatalyst surface. Ray trajectories emitted from a LED set at varying distances from the coated propeller (and at two angles) were simulated. The simulations shown in Figure 5 illustrate the potential photon delivery into the SFPR, highlighting several key parameters; LED viewing angle, propeller configuration, and the resultant light scattering.

Figure 5; YZ profiles of the ray trajectories simulated for irradiation distances ranging from 4 – 7 cm with the associated values of the rays. Only the primary rays are shown for visual clarity.

It is known that increasing the distance of the light source from a catalyst surface results in a decrease in irradiance, however the simulation reported here also provided additional key information on the ray trajectories and the surfaces with which they collide. The viewing angle of the LED and the distance at which it is set from the propeller was the primary factor in determining the percentage of rays which entered the SFPR. Positioning the LED as close as possible to the SFPR (4 cm) ensured 100 % of rays emitted from the source were transmitted through the Pyrex window and into the reaction chamber (Figure

6 (a)). Increasing the distance of the LED however, resulted in a significant drop in rays entering to 92, 65 and 43 % for 5, 6 and 7 cm respectively (Figure 6 (b)).

Figure 6; Images showing the “frozen” rays on the pyrex end plate used in conjunction with a ray detector to count the rays entering the reactor. Irradiation at 4 cm (a) and 7 cm (b) is shown.

In addition to monitoring the percentage of rays entering the reactor, the number of incident rays on the coated propeller surface was also determined (

Figure 7). Interestingly, the ray optics model highlights a significant drop between the rays which enter the reactor to those that strike the propeller. This is a key parameter to consider in any photocatalytic system as it provides a platform for determining efficiency based on the number of ‘absorbed’ photons as opposed to those that are simply delivered.

Figure 7 shows the percentage of rays emitted from the LED which first enter the unit and subsequently the percentage of those rays which go onto either collide or miss the propeller. At the closest distance of 4 cm, only 44 % of the rays that entered the unit were simulated to collide with the propeller surface, while 56 % of those rays entering missed the propeller. These values were based on 100 rays entering the SFPR, but only 44 striking the propeller surface. This value further decreased at a distance of 7 cm, where only 11 rays of the 44 that entered (25 %) were found to reach the propeller. While these calculations are based on 100 rays, a similar ratio was determined when increasing the rays to 10^5 (Tables S1 and S2). Although it is well established that moving a light source further away from a reactor decreases the irradiance, the role this plays in photon loss has been less discussed. It is important to note however, that this only provides an indication of the ray trajectories but does not equate to photons of light absorbed by the catalyst.

Figure 7; Graph showing the percentage of rays which enter the reactor chamber at varying LED distances and the subsequent percentage which “collide” with the propeller and those that do not “strike” the propeller.

While the number of rays (photons) which enter the reactor is a key design detail, it is the irradiance at the surface of a catalyst which determines photocatalytic activity. Simulations were run to determine the correlation between irradiation source distance and the irradiance at the propeller surface. As expected, the irradiance on the surface of the propeller drops significantly as the distance was increased (Figure 8). While these values and trends were expected, the COMSOL model does also highlight the challenge in delivering efficient irradiation when utilising an immobilized reactor which deploys a moving catalyst support. A number of previously reported examples adopt a static support coated with a thin layer. These supports are often a flat plate or the walls of the reactor [14], [15], [34]. To improve mass transfer and light distribution, however, a rotating TiO_2 coated blade is beneficial.

Figure 8; 3-D surface plots of the deposited ray power or irradiance of the light on the catalyst surface for 4 cm irradiation distance at both the initial configuration (a) and the rotated propeller position (b) and also for 7 cm irradiation distance at the initial static position (c) and the rotated propeller position (d).

The irradiance across the surface is significantly higher in the case where the blade is aligned with the LED (Figure 8 (a)), than in the case of the blade rotated 45° with respect to the LED direction (Figure 8(b)). In both cases, there are observed dark spots where the light is unable to reach. Through rotation of the propeller, a more uniform illumination is obtained, along with improved mass transport. In general, a higher number of photons absorbed by a catalyst particle or surface will increase photon-excitation and charged species formation. While this can significantly increase activity, it is dictated by the

presence of absorbed species on the catalyst to begin with. Without sufficient electron donors and acceptors, an increased photon absorption can subsequently result in increased recombination of the electron-hole pair and an inefficient system. The presence of dark spots in this particular system could elude to a similar effect often reported when investigating controlled periodic illumination [35]. Rapidly switching LEDs on and off has been shown to significantly improve photocatalytic activity by controlling excitation and suppressing recombination particularly at lower light intensities [35-37]. Similarly, the rotation of the blade induces a cyclical illumination of the catalyst surface. (Figure 4 and Figure 8).

The work by Li Puma and Yue suggested that theoretical simulation should be coupled with experimental validation, so that unknown microscopic catalytic mechanisms can be fully evaluated. Therefore, in the current investigation, coumarin degradation and conversion to 7-hydroxycoumarin has been used to validate the COMSOL simulation. As previously discussed in the literature [25], [29], [30], coumarin is a chemical probe used for the quantification of OH radicals generated by photocatalytic oxidation.

The conversion of coumarin, subsequent formation of 7-hydroxycoumarin and irradiance as a function of irradiation source distance is shown in Figure 9. As expected, when the irradiation source distance increased, a drop in coumarin conversion and 7-hydroxycoumarin formation was observed which corresponds to both the number of photons (based on COMSOL rays) and catalyst surface irradiance reducing at higher distances. It is noteworthy however, that while computational modelling identified 4 cm as an optimum distance for maximum ray (photon) utilisation and surface irradiance, the experimental work shows that 5 cm may be the optimum distance based on OH• quantification. Despite an increase in the reaction rate of coumarin degradation from 5 to 4 cm, the formation of 7-hydroxycoumarin showed similar values with 5 cm generating slightly higher concentrations; 5.38 and 5.56 μM at 4 and 5 cm respectively. This could be attributed to a higher photo-oxidation rate of 7-hydroxy coumarin at increased light irradiance.

Figure 9; (a) Graph showing the rate of coumarin degradation (R_{cou}) as a function of irradiation distance and compared with measured irradiance values. The insert (b) shows the profile of coumarin degradation (▲) and subsequent formation of OH radicals (●) over time for 4 cm (▲, ●), 5 cm (▲, ●), 6 cm (▲, ●) and 7 cm (▲, ●).

The data collected from both COMSOL simulations and experimental work can be used to determine a photonic efficiency for coumarin conversion for the SFPR. In this case, the photonic efficiency, PE_{cou} , is defined as the ratio between the moles of 'converted' coumarin molecules, R_{cou} , and the moles of absorbed photons on the catalyst surface, γ_{cat} . Photonic efficiencies are useful figures of merit for photocatalytic applications and can provide a platform to compare varying irradiation sources and catalysts. The number of absorbed photons was determined based on the model calculations of the irradiance at the surface of the blades, while the number of converted coumarin molecules was experimentally determined. Equations (1) and (2) were used to determine the values shown in Table 2.

$$\gamma_{cat} = \frac{IA_d}{E_\gamma} \quad (1)$$

Where, γ_{cat} is the moles of photons absorbed by the catalyst film, I is the irradiance at the blade surface (W/m^2), A_d is the surface area and E_γ is the mole of energy in the photon ($\text{J/mol}_{\text{photon}}$). The photon energy can be determined using equation (2):

$$E_\gamma = \frac{h c N_A}{\lambda} \quad (2)$$

Where, h is Planck's constant ($6.6 \times 10^{-34} \text{ m}^2 \text{ kg/s}$), c is the speed of light ($2.99 \times 10^8 \text{ m/s}$), N_A is Avogadro's number ($6.02 \times 10^{23} \text{ mol}^{-1}$) and λ is the peak wavelength of the LED ($3.65 \times 10^{-7} \text{ m}$).

LED distance (cm)	Average irradiance at blade surface (W/m^2)	Moles of photons absorbed at the blade surface (mol/s)	R_{cou} (mol/s)	PE_{cou}
4	293	1.35×10^{-7}	5.00×10^{-9}	0.037
5	221	1.01×10^{-7}	4.50×10^{-9}	0.044
6	123	5.67×10^{-8}	3.67×10^{-9}	0.065
7	77	3.52×10^{-8}	3.17×10^{-9}	0.090

Table 2; Calculated photonic efficiencies for coumarin degradation based on the irradiance values from COMSOL at varying irradiation distance.

Using the same approach, the $PE_{\text{OH}\cdot}$ at varying LED distances were also calculated and are shown in Table 3. Given that OH radicals are the primary reactive species involved with many degradation mechanisms, the coupling of experimental coumarin data with ray optic simulations to determine OH radical photonic efficiency is potentially an advantageous screening method for photocatalytic technology. In relation to both coumarin removal and OH radical quantification, 7 cm shows the highest efficiency. This result is primarily due to the significant differences in surface irradiance as a function of LED distance, while the reaction rate is comparable at all distances. This would suggest that the rate of recombination at shorter distances is significantly higher which is confirmed by the photonic efficiencies increasing as the moles of photons absorbed decreases.

LED distance (cm)	Moles of photon absorbed by the catalyst film on blade (mol/s)	R _{OH•} (mol/s)	PE _{OH•}
4	1.35 x 10 ⁻⁷	7.47 x 10 ⁻¹⁰	0.006
5	1.01 x 10 ⁻⁷	7.72 x 10 ⁻¹⁰	0.008
6	5.67 x 10 ⁻⁸	6.81 x 10 ⁻¹⁰	0.012
7	3.52 x 10 ⁻⁸	6.33 x 10 ⁻¹⁰	0.018

Table 3; Calculated photonic efficiencies for OH• production based on the irradiance values from COMSOL at varying irradiation distance.

The determination of photonic efficiencies in photocatalysis is often challenging, primarily due to the assumptions that are made when calculating the absorption of photons. Reported methods often include using a radiometer to calculate an irradiance (W/m²) at a given distance or using actinometry which calculates a ‘*photon flux*’ entering a reactor. Both approaches were used in this investigation with the comparisons shown in Table 4. The data shows that between the three methods used, the values for moles of photons absorbed by the catalyst surface and PE_{OH•} vary. Despite this however, the trends are similar, with the moles of photons absorbed decreasing and reaction rate, PE_{OH•}, increasing with increasing LED distance. Interestingly, using actinometry to calculate efficiency results in the highest value at PE_{OH•} = 0.38 at a distance of 7 cm. The primary contributing factor in these calculations was the moles of photons absorbed, since the rate of OH radical quantification did not change between the methods. Therefore, it is important to consider which of these methods is the most appropriate to assess the SFPR design. While actinometry is capable of determining the photons which entered the reactor, it is based on the reaction solution being replaced with potassium ferrioxalate and monitoring Fe³⁺ conversion to Fe²⁺, which is not an accurate representation of the catalyst coating on the propeller. Alternatively using a radiometer, which is typically calibrated to a specific wavelength, gives an instant measurement of the irradiance. This value, however, is only relatable to the probe that is used for detection and again is not an accurate representation of the catalyst absorbing the photons. In contrast however, COMSOL determined values of irradiance are based on the number of rays emitted from the source that reach the coated surface, taking the absorption coefficient of the catalyst into account. While these numbers may not be an entirely accurate representation of photons absorbed by the film, they are directly related to the irradiance at the catalyst surface. Based on the data presented here, the irradiance obtained using the COMSOL model provides a less biased estimate of the irradiance at the catalyst surface to determine the photonic efficiency of OH radical generation in a SFPR.

A similar point was also discussed in recent work by Metagif *et al.*, who investigated the use of ‘*blackbody reactors*’ for accurately determining quantum efficiencies [38]. While the work was conducted using a suspended system, they suggested that an internal light source within a blackbody reactor, results in complete photon absorption (when emitted

at a suitable wavelength). By comparison, in the current work, the photonic efficiency (using COMSOL data) was determined based only on the rays that were simulated to strike the propeller, thus providing an irradiance at the catalyst surface.

LED distance (cm)	Moles of photons absorbed by the catalyst film on blade (mol/s)			PE _{OH•}		
	COMSOL	Radiometer	Actinometry	COMSOL	Radiometer	Actinometry
4	1.35 x 10 ⁻⁷	4.34 x 10 ⁻⁸	6.38 x 10 ⁻⁹	0.006	0.017	0.117
5	1.01 x 10 ⁻⁷	2.92 x 10 ⁻⁸	5.16 x 10 ⁻⁹	0.008	0.026	0.150
6	5.67 x 10 ⁻⁸	1.85 x 10 ⁻⁸	3.54 x 10 ⁻⁹	0.012	0.037	0.192
7	3.52 x 10 ⁻⁸	1.35 x 10 ⁻⁸	1.65 x 10 ⁻⁹	0.018	0.047	0.384

Table 4; Comparison of the photonic efficiencies for OH• production based on the three different methods used for calculation, at varying irradiation distance.

The photocatalytic performance at both 4 and 5 cm have been proven to be comparable, despite differences in irradiance and number of rays entering the SFPR. At this point a decision was made to use 5 cm as constant irradiation distance for the work shown in the next section. Whilst 4 cm appears to have improved irradiance it was decided impractical to have the LED positioned so close to the glass plate, especially when future developments such as increased volume (additional number of frames) were considered.

3.2 Effect of propeller rotation speed

Development of immobilised photocatalytic systems represent a significant engineering challenge in providing adequate fluid mixing whilst maintaining high surface area to volume ratios, to facilitate high rates of reaction. Furthermore, the effective delivery of UV radiation to the immobilised catalyst is of extreme importance and as mentioned in the previous section, the rotation of the propeller in the SFPR affects the average irradiation of the catalyst surface. In literature there are few examples of immobilised systems where the reactant mixing is provided by the surface on which the catalyst is supported. For instance, the spinning disk reactor demonstrated by Dionysiou *et al.* [15] who used TiO₂ coated ceramic balls on the disk and investigated the effect of angular velocity over a range of 2 – 41 RPM.

The rotation of the titanium propeller reduces the external mass transfer limitations to improve the efficiency of the SFPR. Simulations were used to model the fluid velocity and mixing generated by the blades in the reaction chamber at varying angular rotation frequency, ω . (Figure 10). The model shows a positive correlation between the rotation speed of the propeller and the velocity of the surrounding fluid about the x-axis, Figure 10 (a) through to (d). Figure 10 (a) (10 RPM) illustrates what appeared to be a completely mass transport limited system, with low fluid velocities throughout the reaction chamber. While increasing the RPM showed a significant increase in fluid velocity around the coated propellers blades, areas with low velocity ('dead zones') were still identified. With an immobilised catalyst, effective delivery of reactant species to the catalyst surface is paramount, especially since the OH• has a short lifespan of 10⁻⁹ s [24]. Therefore, it was essential in the SFPR to improve the external mass transfer coefficient and thereby reduce the thickness of the boundary layer so that the coumarin concentration at the surface of the catalyst is close to its bulk concentration [39].

Figure 10; 3-D multislice plots of the mixing and velocity profiles for the titanium propeller around the x – axis for rotation speeds of 10 RPM (a), 240 RPM (b), 300 RPM (c) and 400 RPM (d).

While the model showed an expected correlation between fluid velocity/ mixing and RPM, subsequently it's the impact of that relationship on photocatalytic activity which is fundamental to determining the efficiency. Therefore, simulations were compared against the experimental rate of coumarin degradation and conversion to 7-hydroxycoumarin to identify the optimum rotation speed (Figure 11). Figure 11 (a) shows the profile of R_{Cou} as a function of propeller rotation, identifying 300 RPM as the optimum speed ($R_{\text{Cou}} = 0.32 \mu\text{M}/\text{min}$). Figure 11 (b) shows a plot $\ln ([\text{Cou}]/[\text{Cou}]_0)$ against irradiation time which indicates the kinetics of coumarin degradation is of (pseudo) first order.

Figure 11; (a) Graph showing the rate of coumarin degradation (R_{cou}) as a function of rotation speed for 0, 10, 240, 300 and 400 RPM. (b) Plot of $\ln([Cou]/[Cou]_0)$ against irradiation time for 0, 10, 240, 300 and 400 RPM.

As previously discussed with photonic efficiencies, coupling experimental data with theoretical simulations can provide more than just a method of validation as the combined results can also give a detailed insight into the efficiency of a photocatalytic system. Equations were used to calculate the external mass transfer coefficient, k_c , based upon the numerical data with the results shown in

Table 5. Equation (3) shows the corresponding rotational speed of the propeller considered as the simplest form of average fluid velocity in the surrounding rotating domain, with directly comparable average fluid velocities evaluated using COMSOL, where the radius of the propeller, $r_p = 0.01$ m.

$$v_{\text{rot}} = \left(\frac{2\pi \text{RPM}}{60} \right) r_p \quad (3)$$

Equations (4), (5) and (6) were then used to calculate the Reynolds number, Re, the Sherwood number, Sh and the external mass transfer coefficient, k_c [39].

$$\text{Re} = \frac{v_{\text{rot}} \rho d_p}{\mu} \quad (4)$$

$$\text{Sh} = 2 + 0.6\text{Re}^{0.5}\text{Sc}^{1/3} \quad (5)$$

$$k_c = \frac{\text{Sh}D_{\text{cou}}}{d_p} \quad (6)$$

In the previous expressions, the Schmidt number, $\text{Sc} = 1252.50$, the density, $\rho = 1000 \text{ kg/m}^3$, the diameter of the propeller, $d_p = 0.02 \text{ m}$, the dynamic viscosity, $\mu = 1.002 \times 10^{-3} \text{ Pa}\cdot\text{s}$, and the diffusivity of coumarin, $D_{\text{cou}} = 8 \times 10^{-10} \text{ m}^2/\text{s}$.

RPM	V_{rot} (m/s)	Reynolds number	Sherwood Number	Mass transfer coefficient k_c (m/s)	R_{cou} (μM/ min)
0	0	0.00	2.00	8.00×10^{-8}	0.12
10	0.01	208.92	95.48	3.82×10^{-6}	0.24
240	0.25	5013.97	459.97	1.84×10^{-5}	0.29
300	0.31	6267.47	514.02	2.06×10^{-5}	0.32
400	0.42	8356.62	593.23	2.37×10^{-5}	0.30

Table 5; Table showing the maximum fluid velocity for varying rotation speeds of the titanium propeller. The associated Reynolds and Sherwood numbers are also shown alongside the mass transfer coefficient k_c and compared against the rate of coumarin degradation.

A key observation shown from the data at 10 RPM is that rotation of an immobilised propeller even at laminar flow can significantly improve the performance of a photocatalytic system despite still being mass transfer limited. In Figure 10 (a) the COMSOL model displays a minimal average fluid velocity and V_{rot} being calculated as 0.01 m/s. Based on the simulations at this speed, this SFPR was expected to be mass transport limited despite an increase in k_c , however R_{cou} when RPM = 0, gives an indication that perhaps it is more than simply just an improvement in external mass transfer. Going from a static system to 10 RPM showed a 2-fold increase in R_{cou} from 0.12 to 0.24 $\mu\text{M}/\text{min}$, which would not be expected from the velocity profiles shown by the model. Considering the physical rotation of the propeller, which is the catalyst support, and the positioning of the LED, the increase in R_{cou} (at 10 RPM) was likely primarily a result of increasing the irradiated surface area of the catalyst. Rotating the blades, even at slow speeds, exposed twice as much catalyst surface to the LED which created a more favourable irradiated surface area to volume ratio with accelerated OH radical formation.

The second key observation is that beyond 10 rpm, the relationship between RPM and R_{cou} appeared to be predominantly determined by reduced mass transfer limitations with turbulent flow being established. An increase in R_{cou} from 0.24 to 0.32 $\mu\text{M}/\text{min}$ from 10 - 300 rpm can be attributed to a more than fourfold increase in k_c . At 300 RPM the modelling results and the experimental work correlate directly, as improved fluid velocity and mixing within the reactor was reflected in increased coumarin degradation as a result of reduced boundary layer thickness. Similar trends are seen in the OH radical generation (Figure S1). Beyond this, despite the mass transfer coefficient being further increased to 2.37×10^{-5} m/s, a 6.3 % drop in R_{cou} was recorded, which highlights the need for both approaches (theoretical and experimental) to be used when fully investigating the performance of a reactor. At 400 RPM, mass transfer limitations are no longer predominant with additional parameters becoming more relevant; photon absorption, coumarin adsorption onto the surface of the catalyst, internal mass transfer and reactant concentration. At higher rotational speeds, it was likely that both photon absorption and contact time between coumarin and the catalyst surface reduced, which resulted in a drop in R_{cou} .

4. Conclusions

A novel immobilised photocatalytic system, utilising a titanium “bladed” propeller has been designed and evaluated using both COMSOL Multiphysics® 5.3a and experimental validation. COMSOL geometrical ray optics has been shown as a capable method of predicting the distribution of light within a reactor, highlighting the link between reactor geometry and irradiance at the catalyst surface at varying irradiation distances. Irradiance calculations from COMSOL were compared with measurements from a radiometer and experimental actinometry, highlighting similar trends but variation in results due to methodology. Experimental coumarin degradation has shown 4 and 5 cm to be comparable for the SFPR with the highest OH radical concentration (5.56 μM) at 5 cm.

Increased performance at these distances has been linked not only to irradiance but the ray distribution with 100 and 92 % of rays entering the reactor at 4 and 5 cm respectively.

Modelling of fluid velocity and mixing within the SFPR presented the mixing patterns over a range of 0 – 400 RPM, with the highest fluid velocity of 0.42 m/s at 400 RPM indicating optimal performance with reduced external mass transfer limitations however this was not the case, with experimental data proving 300 RPM to be the optimal speed for both coumarin degradation and OH• production, with the highest R_{cou} of 0.32 $\mu\text{M}/\text{min}$. These results demonstrate the importance of coupling modelling with experimental validation to provide valuable information around the kinetics of a reaction.

Supporting Information

(Table S1) Number of rays entering the reactor and striking the propeller as evaluated in COMSOL through use of a ray detector, based on 100 rays emitted from the light source;
(Table S2) Number of rays entering the reactor and striking the propeller as evaluated in COMSOL through use of a ray detector, based on 10^5 rays emitted from the light source;
(Figure S1) Graph showing the formation of OH radicals over time for the varied rotation speeds of the titanium propeller (0, 10, 240, 300 and 400 RPM)

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