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Communication
Photocatalytic OH radical formation and quantification over TiO$_2$ P25: producing a robust and optimised screening method
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Graphical abstract

Photocatalytic oxidation of coumarin to 7-hydroxycoumarin was used in order to identify the optimum conditions and the potential limitations of a photocatalytic screening method.
The development of photocatalytic technology has grown significantly since its initial report and as such, a number of screening methods have been developed to assess activity. In the field of environmental remediation, a crucial factor is the formation of highly oxidising species such as OH radicals. These radicals are often the primary driving force for the removal and breakdown of organic and inorganic contaminants. The quantification of such compounds is challenging due to the nature of the radical, however indirect methods which deploy a chemical probe to essentially capture the radical have been shown to be effective. As discussed in the work presented here, optimisation of such a method is fundamental to the efficiency of the method. A starting concentration range of coumarin from 50 μmol/L to 1000 μmol/L was used along with a catalyst loading of 0.01 g/L to 1 g/L TiO₂ to identify that 250 μmol/L and 0.5 g/L TiO₂ were the optimum conditions for production. Under these parameters a maximum production rate of 35.91 μmol/L (R_{max} = 0.4 μmol/L OH• min⁻¹) was achieved which yielded at photonic efficiency of 4.88 OH• moles photon⁻¹ under UV irradiation. The data set presented also highlighted the limitations which are associated with the method which included: rapid exhaustion of the probe molecule and process inhibition through UV light saturation. Identifying both the optimum conditions and the potential limitations of the process were concluded to be key for the efficient deployment of the photocatalytic screening method.

The advancements in both catalytic materials and reactors has driven the field of photocatalysis for the past four decades. As a result, the effective rapid screening and evaluation of photocatalytic components has become paramount. Traditionally this has been done with model compounds or fingerprint chemicals which provide an indication on the performance and activity of reactors and catalysts [1–6]. The choice of compound, however, is not always suitable for the desired application. In environmental remediation, the primary mechanism involved in many processes is the formation of hydroxyl (OH) radicals. These non-selective photon-induced radical species are capable of oxidising a range of compounds such as hydrocarbons, toxins, dyes and other pollutants [7–13]. In particular, these species can have lethal effects on bacteria and other intracellular molecules resulting in physiological alterations, growth delay of bacterial membranes and subsequent in growth inhibition [14].

OH radicals are a highly reactive species and as a consequence, have a very short lifespan of 10⁻⁹ s in one system, [15], making them difficult to quantify directly. Therefore the indirect quantification is generally favoured via a number of methods including emission spectroscopy, laser induced fluorescence, electron spin resonance, spin trap and chemical probes or quencher [16]. The use of a chemical probe presents an approach which is cheap, robust and capable of providing rapid data for screening processes. To date, compounds such as terephthalic acid, coumarin and humic acid [17] have been deployed for this purpose [15,18–21]. The selection of the probe is crucial to ensure the accurate measurement of the radical species. Ideally it should involve a relatively simple chemical reaction that yields a sole product which is easily detectable and directly linked to OH radical formation. As reported in the literature, coumarin acts as an excellent probe molecule for measuring OH radical formation due to the production of 7-hydroxycoumarin via a simple hydroxylation reaction. While a number of products can be produced depending on the location of the OH ion to coumarin, 7-hydroxycoumarin is the only product which is fluorescent.

Radical species measurements via coumarin for photocatalytic screening has been reported for various applications [15,16,20,22,23]. In 2017, Nagarajan et al. [21] deployed the method for the quantification of OH radicals from a range of both ultra violet (UV) and visible activated catalysts. The investigation showed titanium dioxide (TiO₂) P25 to generate the highest number of OH radicals and confirmed that without sufficient band potentials, minimal OH radicals was seen over catalysts C₃N₄, WO₃ and SrTiO₃. Generally, there has been little research into the effect of catalyst loading on a range of coumarin concentrations with a view towards OH radical production. Hajnalka Czili [15] investigated an initial range of coumarin concentrations from 50-2000 μmol/L, but only carried out further experiments using 100 μmol/L coumarin. These experiments used 1 g/L TiO₂ loading only, concluding that coumarin is an applicable chemical probe when detecting and measuring OH radicals [15]. Xiang et al. [16] used a 100 μmol/L coumarin concentration with a high loading of TiO₂ at 5 g/L to confirm that pH and the phase structure of TiO₂ had a significant influence on the production rates of OH radicals. In addition, Jie Zhang [23] also used a high loading of 4.2 g/L TiO₂ and 100 μmol/L coumarin solution, to show the OH radical formation on various kinds of TiO₂ modified for visible light activation.

Following on from our previous work [21], reported herein is the impact of both catalyst loading and coumarin starting concentration on OH radical quantification with a view towards producing an optimised system for screening. While the optimum loading of a catalyst has often been determined for various applications, to date the impact on OH radical formation via coumarin has not. Also shown are the photonic efficiencies with a view to establishing a robust screening method for researchers in this field.

The following materials were all used as received: TiO₂ P25 (Evonik), coumarin (Tokyo Chemistry Industry) and 7-hydroxycoumarin (Tokyo Chemistry Industry). The concentrations of coumarin investigated were 1000, 500, 250, 100 and 50 μmol/L. The range of catalyst loadings investigated were 0.01, 0.05, 0.1, 0.5 and 1 g/L. Millex syringe filters with a pore diameter of 0.22 μm were used to filter the samples taken during the experiments in order to remove the suspended photocatalyst prior to analysis.
All the experiments were performed in a screw cap bottle with a maximum volume of 250 mL. Each experiment used a reaction volume of 100 mL of coumarin solution with the various catalyst loadings. All experiments were performed without modification to the pH. The bottles were stirred using a magnetic plate and stirrer bar. The bottles were placed at a distance of 11 cm away from a 36 W compact florescent non-integrated UV lamp (Philips, CLEO). Experiments using TiO\textsubscript{2} UV light and coumarin solutions were carried out to identify the quantity of 7-hydroxycoumarin formed and in turn, the quantity of OH radicals formed during the photocatalytic reaction could be determined. At dedicated time intervals samples (1.5 mL for coumarin and 3.5 mL for 7-hydroxycoumarin) were removed for spectroscopic analysis.

Coumarin analysis was performed using a Cary 300 UV/visible spectrophotometer set at wavelength of 277 nm and scan rate 199.8 nm/min with a quartz cuvette (transmittance from 200-2500 nm). The concentration of coumarin was determined based on comparison to a calibration graph of known concentrations.

A PerkinElmer LS 50B Luminescence Spectrometer fluorimeter was used to analyse the concentration of 7-hydroxycoumarin. The excitation wavelength was set at 332 nm and the emission wavelength was set at 456 nm. The excitation and emission slit width was 4 mm and the scan rate was 200 nm/s. The luminescence intensity of 7-hydroxycoumarin was measured at 456 nm. The concentration of 7-hydroxycoumarin was determined based on methods reported in the literature [15,16,20,23,26].

To accurately monitor the spectral characteristics of the lamps and the photonic efficiency of the system, the photon flux was determined using the potassium ferrioxalate actinometrical method [24,25]. The photon flux was determined by replacing the photocatalytic solution with actinometry solution. The photonic efficiency was then determined based on the calculated photon flux along with Eq. 2.

\[
\text{Photonic efficiency} = \frac{\text{Reaction rate (mole min}^{-1})}{\text{Photon flux (Jillinstein L}^{-2}\text{min}^{-1})} \quad (2)
\]

Currently reported in the literature is the determination of OH radicals formed over only a small concentration range of chemical probes and catalysts [15,16,20,23,26]. Furthermore, these ranges were conducted under different operating parameters and by different groups, thus making the identification of optimum conditions challenging. Previous research investigating coumarin degradation has examined coumarin concentrations as low as 100 \(\mu\text{mol/L}\) and TiO\textsubscript{2} loadings as low as 0.2 g/L [20,26]. The data set presented here investigated a range of coumarin concentrations and TiO\textsubscript{2} loadings that span beyond those previously researched, with a view towards developing a robust data set that can aid researchers in this field. In addition to establishing optimum operating conditions for screening OH forming catalysts, limitations with this method have been identified.

The impact of coumarin starting concentration on OH radical formation is shown in Fig. 1a when the catalyst loading was set at 0.5 g/L. At a starting concentration of 250 \(\mu\text{mol/L}\), optimal OH radical formation was recorded with a maximum at 35.91 \(\mu\text{mol/L}\). In regards to using a lower concentration, the rapid conversion of coumarin to 7-hydroxycoumarin and the subsequent oxidation of 7-hydroxycoumarin leads to a peak production of OH radicals within 20 min and 45 min for 50 and 100 \(\mu\text{mol/L}\) respectively. While this was an observed expectation, increasing the starting concentration further, did not follow an expected trend. At higher concentrations of 500 and 1000 \(\mu\text{mol/L}\), a peak production of OH radical was not observed in the irradiation time frame, however, a significant drop in formation was noted. A rate of 0.12 and 0.073 \(\mu\text{mol L}^{-1}\text{min}^{-1}\) was recorded for 500 and 1000 respectively, as oppose to the high rate of 0.3 \(\mu\text{mol L}^{-1}\text{min}^{-1}\) for 250 \(\mu\text{mol/L}\). This drop was largely thought to be due to two factors: competition for photon absorption and over concentration of the probe molecule. As shown in Fig.1b, the spectral output of the 36 W lamp used overlaps with the absorption profile of coumarin. Therefore, at higher concentrations of the probe molecule, it was expected that an increased number of photons would be absorbed before being consumed in the photocatalytic reaction. This observation has previously been reported by Czili et al. [15], who also found photocatalytic activity dropped at higher concentrations of coumarin. In addition, the drop could simply be attributed to the concentration of coumarin in the system being greater than the catalyst was capable of removing in the given time frame.
This data clearly shows that establishing the correct starting concentration is paramount for efficiently deploying this screening method. As this process was acting as an indirect method for quantification of a radical species, it was essential that the data was an accurate representation of that compound. The data shown in Fig. 2 highlights two limitations; probe molecule exhaustion and process inhibition through UV light saturation. The exhaustion of the probe molecule results in a peak formation rate being reached within a short time frame, Fig. 2. Interestingly, steady state OH radical production was only achieved with higher concentrations (500 and 1000 µmol/L) with 250 µmol/L showing a drop in reaction rate suggesting that peak production was close to being reached. This is a key observation for screening purposes, as steady state production over a prolonged irradiation period would be the ideal scenario. Furthermore, as Fig. 1a and Fig. 2 depict, the data suggests that OH radical production was decreasing with regards to starting concentrations of 50 and 100 µmol/L, which was not accurate. Only the probe molecule was reducing, while OH radical formation should in theory be maintained presuming UV light, catalyst and OH ions are still present.

Alternatively, preventing exhaustion by deploying an overly concentrated solution leads to UV light saturation and process inhibition. Both of these factors can result in an inaccurate OH radical estimation. It is noteworthy, however, that while 250 µmol/L provides the optimum starting concentration for OH radical formation, it can also be considered as the ‘minimum OH radical production value’. While light saturation was at a minimum, it would not be feasible to make the assumption that all OH radicals generated are used by coumarin as the system may still be dictated by mass transport limitations. Therefore, based on this data set it can be stated that deploying this method of quantification can provide accurate data on a minimum value being produced when operated at optimum conditions.

The impact of catalyst loading has been frequently reported in the literature with the optimum concentration typically being 0.5-1 g/L [1,15,27,28]. This was also confirmed by the data that is shown in Figure 3, which identifies 0.5 g/L as the optimum loading for OH radical formation with a peak at 35.91 µmol/L. At a 1 g/L loading, a drop in 7-hydroxycoumarin formation was observed which was expected and was predicted to continue with increasing loadings. This was simply due to higher TiO₂ loadings creating increased turbidity and thus decreasing light penetration and increasing photon scattering. Interestingly, this limitation is one which is typically photocatalytic and not necessarily related to the coumarin screening method. As such, Figure 3 highlights the ability of the method to effectively screen catalysts at lower concentrations (0.01 g/L) and still see significant OH radical formation. To date, this has not been reported in the literature as the deployment of low level TiO₂ loadings is often overlooked for photocatalytic applications. Based on this data set, however, the reaction rate for 0.01 g/L can be given as 11.08 µmol/L.OH• g⁻¹ TiO₂ min⁻¹, which is significantly higher than 0.5 g/L which gives only 0.6 µmol/L.OH• g⁻¹ TiO₂ min⁻¹. This observation highlights the impact that catalyst loading can have on photocatalytic OH radical formation.
The results shown in Fig. 4 further confirm that the optimum operating conditions for this OH radical screening method was a starting concentration of 250 μmol/L with a catalyst loading of 0.5 g/L. Furthermore, this data set stresses the need to fully optimise any photocatalytic screening method. The primary driving force for photocatalytic environmental remediation is typically OH radical induced oxidation. Therefore, identifying the optimum conditions for the generation of these species is essential. While coumarin to 7-hydroxycoumarin is a rapid chemical conversion, which can be coupled with a simple and efficient spectroscopic measurement method, there are limitations to the approach. The first being the UV absorption of coumarin which can inhibit photocatalysis. The second is the exhaustion of coumarin which subsequently leads to the oxidation of 7-hydroxycoumarin.

Fig. 5a depicts coumarin degradation and OH radical production using 0.5 g/L TiO₂ loading and 100 μmol/L coumarin. This graph highlights the point at which coumarin becomes consumed and the consequent reduction of 7-hydroxycoumarin being formed. The 7-hydroxycoumarin that is produced at the start of the experiment is also degraded by the UV light and other species that could be present, hence the large decrease in 7-hydroxycoumarin seen in the experiment. Fig. 5b depicts the highest OH radical production seen in the experiment using 0.5 g/L TiO₂ loading and 250 μmol/L coumarin. This graph shows that this higher coumarin concentration allows OH radicals to still be formed, even with the rapid degradation of coumarin.

The photonic efficiencies for both coumarin concentration and OH radical formation were also determined for the experimental data set and are shown in Table 1 and Table 2. Interestingly, over the concentration range, the peak efficiency was recorded for 1000 μmol/L at 24.41 moles photon⁻¹, with 250 μmol/L being lower at 21.66. In addition to this, however, the peak OH radical formation clearly shows the expected trend with the peak photonic efficiency (4.88) being recorded for 250μmol/L. These two observations may actually suggest that despite an efficient conversion of coumarin at 1000 μmol/L, subsequently the relative OH formation does not match. Therefore, the ratio of coumarin to 7-hydroxycoumarin at varying concentrations could vary from the assumed 6.1% reported in the literature [23]. This is currently the focus of on-going work.
Table 1: the calculated photonic efficiencies for coumarin conversion and OH radical formation over various coumarin starting concentrations at a TiO\(_2\) loading of 0.5 g/L where \(R_{\text{max}}\) is the peak reaction rate.

<table>
<thead>
<tr>
<th>Coumarin Concentration (µmol/L)</th>
<th>Coumarin conversion ((\times 10^4 \text{moles/min}))</th>
<th>Photonic efficiency ((\text{coumarin mole photon}^{-1}))</th>
<th>OH radical formation ((\times 10^4 \text{moles/min}))</th>
<th>OH radical photonic efficiency ((\text{OH mole photon}^{-1} \text{gTiO}_2^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>0.0637</td>
<td>10.07</td>
<td>0.5</td>
<td>7.90</td>
</tr>
<tr>
<td>100</td>
<td>0.817</td>
<td>12.92</td>
<td>0.466</td>
<td>7.75</td>
</tr>
<tr>
<td>250</td>
<td>1.370</td>
<td>21.66</td>
<td>0.31</td>
<td>4.88</td>
</tr>
<tr>
<td>500</td>
<td>1.256</td>
<td>19.85</td>
<td>0.119</td>
<td>1.88</td>
</tr>
<tr>
<td>1000</td>
<td>1.544</td>
<td>24.41</td>
<td>0.079</td>
<td>1.25</td>
</tr>
</tbody>
</table>

As expected, across the catalyst loading range used in this study, the peak photonic efficiency (4.88) was observed when using 0.5 g/L. It was interesting to note however, that if the loading of active material is factored into the calculation that the order of efficiency is reversed with 0.01 g/L being significantly more active than others, Table 2.

Table 2: the calculated photonic efficiencies for OH radical formation over various TiO\(_2\) loadings at a coumarin starting concentration of 250 µmol/L.

<table>
<thead>
<tr>
<th>Catalyst loading (g/L)</th>
<th>OH radical (R_{\text{max}}) ((\times 10^4 \text{moles/min}))</th>
<th>OH radical photonic efficiency ((\text{OH mole photon}^{-1}))</th>
<th>OH radical photonic efficiency ((\text{OH mole photon}^{-1} \text{gTiO}_2^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.01</td>
<td>0.1008</td>
<td>1.59</td>
<td>139</td>
</tr>
<tr>
<td>0.05</td>
<td>0.1341</td>
<td>2.12</td>
<td>42.4</td>
</tr>
<tr>
<td>0.1</td>
<td>0.2408</td>
<td>3.81</td>
<td>38.1</td>
</tr>
<tr>
<td>0.5</td>
<td>0.3089</td>
<td>4.88</td>
<td>9.76</td>
</tr>
<tr>
<td>1</td>
<td>0.3058</td>
<td>4.83</td>
<td>4.83</td>
</tr>
</tbody>
</table>

In conclusion, the results shown in this investigation highlight the importance of determining optimum conditions for the development of an efficient photocatalytic screening method. At a starting concentration of 250 µmol/L, OH radical quantification can be accurately measured to provide a ‘minimum produced value’ of 35.91 µmol/L. The impact of catalyst loading was as expected with peak production occurring at 0.5 g/L TiO\(_2\). Increasing the loading further resulted in a drop in OH radical formation, however the data set did demonstrate that even at lower concentrations of TiO\(_2\) (0.01 g/L) OH radicals are not only produced but are quantifiable. In the view of the authors, these results are key to establish an efficient and robust screening method which has potential to be deployed to not only OH radical producing catalysts but also photocatalytic reactors.

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References