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Abstract

Photocatalytic remediation technology has been shown to be a favorable approach for the removal of a range of environmental pollutants in water treatment. While this approach can often achieve complete degradation, often overlooked are reaction intermediates that are potentially as harmful as the original parent compound. In the case of photocatalytic oxidation of the herbicide 2-methyl-4-chlorophenoxyacetic acid (MCPA), we have recently shown that 4-chloro-2-methylphenol (CMP) is formed as the primary intermediate. To ensure the continued development of the technology, it is crucial to ensure the removal of both MCPA and CMP can be achieved by photocatalysis. Reported here is the enhanced photocatalytic removal and subsequent suppression of MCPA and CMP respectively, by the addition of small quantities of H_2O_2 . While the addition of H_2O_2 often accelerates degradation rates (*via* increased OH radical production), it was found to restrict the formation of CMP in this study through competitive adsorption at the surface of TiO_2 . Based on the combination of MCPA removal coupled with suppressed CMP formation, 0.5 % H_2O_2 was determined to be an optimal loading for the process. Under these conditions 100 % MCPA removal was achieved (to the limit of HPLC detection) after 45 mins irradiation at a degradation rate of $\sim 1 \text{ mg L}^{-1} \text{ min}^{-1}$ ($\eta_{\text{photon}} = 4.4$), which also resulted in a ~ 83 % reduction in CMP formation when compared to a system with no H_2O_2 present.

Keywords:

Photocatalytic remediation, 2-methyl-4-chlorophenoxyacetic acid, hydrogen peroxide, low power irradiation, photoreactor technology

1. Introduction

The growth of the agricultural sector to meet global population rise was inevitably accompanied by the overuse of herbicides and pesticides, which in turn resulted in increased contamination of water bodies (Myers et al., 2016). This has put a significant strain on waste-water and drinking water treatment plants that need to achieve rapid and efficient removal of pollutants such as MCPA, which can often not be achieved with traditional methods such as commercial activated carbon filters (Derylo-Marczewska et al., 2010; Gimeno et al., 2003; Macaulay, n.d.; Taylor & WATER), 2016). Advanced Oxidation Processes (AOPs) such as photocatalysis present an environmentally benign and low energy alternative to deal with the issue (Bethi et al., 2016; Boczkaj & Fernandes, 2017; Byrne et al., 2017; Kelly et al., 2019). Upon absorption of photons, photocatalysts can generate powerful radicals ($\text{OH}\cdot$ and $\text{O}_2\cdot^-$), which can destroy organic pollutants *via* an oxidation reaction. In addition, direct oxidation can also occur *via* the photogenerated holes in the valence band reacting with pollutants adsorbed onto the photocatalyst surface. When aiming to deploy photocatalytic technology in large scale water treatment, an in depth understanding of the degradation mechanism is of paramount importance.

Previously, we reported on the impact of adjusting the pH on photocatalytic MCPA degradation with a view towards revealing the mechanism at the catalyst surface (Kelly et al., 2019). It was shown that in aqueous suspensions of TiO_2 (pH=6.2), the negatively charged pollutant (pKa=3.73) is electrostatically attracted to positively charged catalyst surfaces. This strong surface binding facilitated the conversion of MCPA to its primary

intermediate, 4-chloro-2-methylphenol (CMP). The study found that adjusting the pH towards either further acidic or basic conditions not only impacted the conversion of MCPA to CMP, but also the overall removal of both pollutants.

In view of our recent study, it is crucial to ensure that complete and rapid removal of both parent and any intermediate pollutants has been achieved. Previously, photocatalytic studies have found that the use of H_2O_2 as an additive can aid in ascertaining this through increasing $OH^\bullet$ production *via* electron scavenging (Cornish et al., 2000; Elmolla & Chaudhuri, 2010; Tseng et al., 2012; Y. Wang et al., 2013; Wong & Chu, 2003). This process can occur *via* two mechanisms; H_2O_2 can act as a direct electron acceptor at the conduction band of the catalyst instead of O_2 , which has been reported to be the more thermodynamically favorable reaction ($E^0 = 0.72$ for H_2O_2 reduction, $E^0 = -0.13$ for O_2 reduction) (Equation 1) (Cornish et al., 2003; Jaeger and Bard, 1979). Alternatively, any H_2O_2 that is not reduced at the conduction band is free to react with the superoxide that is generated when O_2 accepts the conduction band electron (e_{CB}^-), (Equation 2 and 3). Both processes can occur along with the standard oxidation of OH^- by the positive hole in the valence band (h_{VB}^+) to increase the number of OH radicals formed. Direct oxidation of H_2O_2 can also occur *via* reaction with photogenerated holes (and OH radicals), which results in the generation of the superoxide anion radical.

To date, a primary focus of H_2O_2 as an additive to photocatalytic processes has been on enhancing the removal of specific pollutants. This is often monitored with techniques such as chemical oxygen demand (COD) to determine the concentrations of all chemicals (in-organic and organic) within photo-systems (Affam et al., 2013; Thind et al., 2018; Guimarães Barrocas et al., 2018). A limitation to such an approach, however, is the sensitivity of COD measurements to ensure complete or near complete removal of a pollutant. Moreover, any information on the specific formation and degradation of intermediates in the reaction is commonly overlooked. In a lot of cases the information on the formation and potential degradation of these intermediates can be of the upmost importance as they can be environmentally damaging and more toxic than their parent compounds (Escher & Fenner, 2011; W.-L. Wang et al., 2018).

Therefore, this study investigates the impact of H_2O_2 on the photocatalytic oxidation of MCPA and formation of CMP in a fluidised reactor under low power LED irradiation. In contrast to previous reports that have used H_2O_2 as an additive to accelerate the degradation of a pollutant, shown here is photocatalytic enhancement through the suppression of harmful intermediates compounds. Despite the increase in the number of papers reports MCPA as a model in photocatalytic applications, to date there has been no report on the effects of H_2O_2 .

2. Materials and methods

2.1 Materials

HPLC grade solvents, 2-methyl-4-chlorophenoxyacetic acid (MCPA), 4-chloro-2-methylphenol (CMP), and H_2O_2 (30 wt. % in H_2O) were purchased from Sigma Aldrich (Gillingham, UK). TiO_2 P25/20 was purchased from Evonik (Milton Keynes, UK). All materials were used as received.

2.2 Photocatalytic Reactor

A propeller fluidised photoreactor (PFPR) was used for the photocatalytic experiments performed in this study, which has been described elsewhere (Skillen et al., 2016). The unit had a total capacity of 200 mL with a typical operating capacity of 100 mL. Briefly, the unit is constructed of an annular quartz glass body with a stainless-steel top and bottom flange. A propeller driven by a Bilge pump motor was fitted to the bottom to provide suitable mixing of the herbicide-catalyst suspension. The propeller was constructed from stainless steel 316 and had four blades angled at 45° to provide optimum mixing conditions. The bilge pump motor was controlled via a variable DC power supply (Model 72-10480, Tenma) that operated in the range 0-12 dcV. The typical operational voltage was 3.5 dcV, which gave a propeller speed of 1,200 rpm.

Irradiation of the unit was provided by a UV-LED (LZ1-10UV00-0000, LED Engin Europe) mounted onto a 50×20 mm heatsink (ILA-HSINK-STAR, Intelligent LED solutions), which had a peak wavelength of 370 nm and a viewing angle of 70° . A variable DC power supply supplied the voltage to give a $V_F = 3.5$ dcV and $I_F = 0.3$ A,

which gave an overall power of 1.05 W. The LED was positioned directly above the PFPR and provided direct irradiation down the centre of the PFPR. The reactor system is depicted in Figure 1.

Figure 1. Image of the PFPR under irradiation from a low power UV-LED

2.3 Photocatalytic procedure

In the present study the PFPR was deployed to monitor the degradation of MCPA and formation of CMP over a range of H_2O_2 concentrations. MCPA degradation was performed in the PFPR over P20 TiO_2 and a single LED. In a typical experiment, 0.5 g L^{-1} loading of catalyst was dispersed in 100 mL of aqueous medium containing 50 mg L^{-1} MCPA and distilled water. Initially the contents of the PFPR were equilibrated for 20 min in the dark (based on dark control experiments – see Figure S4) before illuminating with the LED. Dark (no light with catalyst) and light controls (no catalyst with light) were

performed for all experiments during the investigation. Samples (1 mL) were taken at dedicated time intervals and all samples were centrifuged to remove the suspended catalyst from the solution. To accurately monitor the spectral characteristics of the lamps and the photonic efficiency (η_{photon}) of the system, the photon flux was determined and calculated to be 8.19×10^{-7} moles of photons per min. Based on the photon flux, the η_{photon} was calculated using Equation 4 and is described as moles of MCPA degraded per moles of photons delivered. The LED irradiance was also determined at two points within the reactor; at the top of the reaction suspension during mixing (12.15 mW cm^{-2}) and at the base of the unit where the propeller was located (1.55 mW cm^{-2}).

Equation 4

$$\eta_{\text{photon}} = \frac{\text{MCPA degradation (mole of MCPA L}^{-1} \text{ min}^{-1})}{\text{Photon flux (moles of photon L}^{-1} \text{ min}^{-1})}$$

Where the '*MCPA degradation*' was the reaction rate, determined as the number of moles of MCPA degraded over a given irradiation time (or where removal beyond the limit of detection was achieved), as shown in Equation 5.

Equation 5

$$\text{MCPA degradation} = \frac{C_0 - C_x}{t \text{ (min)}}$$

Where ' C_0 ' is the initial concentration (moles L^{-1}), ' C_x ' is the concentration (moles L^{-1}) after 120 mins of irradiation or was given as ' 0 ' in the instance where removal beyond the limit of detection has been achieved and ' t ' is the irradiation time frame or time taken to achieve removal beyond the limit of detection.

The influence of H_2O_2 on the photocatalytic degradation was studied in the range of 0-2 v/v%. The pH of a 50 mg L^{-1} MCPA solution (pH=3.8) was unadjusted during experiments. All experiments were performed in duplicate throughout the investigation. All data shown herein are based on calculated mean values with standard deviation also determined.

MPCA and CMP were both monitored using an Agilent 1100 HPLC system, equipped with a photodiode array (PDA) UV-Vis and a fluorescence detector (FLD) recording traces at 230 nm and 230 nm (Ex.) - 320 nm (Em.) for MCPA and CMP respectively (see Figure S2). Full details of the analytical method can be found in our previous report (Kelly et al., 2019).

3. Results & Discussion

3.1 Effect of H_2O_2 on MCPA degradation

The impact of H_2O_2 on the degradation of MCPA is shown in Figure 2, which provides an interesting indication that multiple processes were capable of significantly

influencing the overall process (supported by Figure S2-S4). Focusing on the photocatalytic process initially, a trendline was fitted for the 0 % H_2O_2 data series, which allows the impact of increasing concentrations to be visualized more clearly. In the initial stages of irradiation (up to 10 mins), the addition of H_2O_2 (up to 0.5 %) increased the photocatalytic rate from $3.33 \text{ mg L}^{-1} \text{ min}^{-1}$ (at 0 %) to a peak of $4.17 \text{ mg L}^{-1} \text{ min}^{-1}$ at 0.05 % H_2O_2 . As the irradiation time reached 20 and 45 mins, however, more comparable rates between 0 – 0.5 % H_2O_2 were noted. In contrast to this, at 1 and 2 % H_2O_2 , the photocatalytic rate was noticeably lower with a more significant decrease observed at 2 %; a reduction from 3.33 to $2.35 \text{ mg L}^{-1} \text{ min}^{-1}$ after 10 mins followed by 2.11 to $1.54 \text{ mg L}^{-1} \text{ min}^{-1}$ after 20 mins. Interestingly, the addition of higher H_2O_2 concentrations appeared to inhibit photocatalytic MCPA degradation, as opposed to accelerating it, which is often the case for organic pollutants in such a system (Cornish et al., 2000; Qamar et al., 2006; Wong & Chu, 2003). With a high loading of H_2O_2 (≥ 1 %), a drop in the reaction rate was expected, primarily as result of the surface of TiO_2 becoming saturated. At lower concentrations, however, an increased reaction rate was expected as a result of the number of OH radicals produced per photon delivered also increasing. Crucially, this would also suggest that the addition of H_2O_2 has an impact on degradation through the interaction between the TiO_2 surface and MCPA. It has previously been reported that H_2O_2 can cause TiO_2 to coagulate while in suspension and as result decrease the available surface area (Cornish et al., 2000). H_2O_2 adsorbing to the TiO_2 surface can influence the surface charge minimising the repulsive forces taking place between TiO_2 nanoparticles, which subsequently allows Van der Waals forces between particles to produce agglomerations. The formation of larger TiO_2

200 agglomerates as a result of higher H_2O_2 concentrations could account for the decrease
201 in reaction rates seen in Figure 2 at 1 and 2 % H_2O_2 .

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Figure 2: (a) Removal of MCPA as a function of H₂O₂ (%) and time where ● is 0 %, ● is 0.01 %, ● is 0.05 %, ● is 0.1 %, ● is 0.5 %, ● is 1 % and ● is 2 %. UV-LED irradiation was started when Time (min) = 0, with the dark equilibrium time depicted as -20 mins to 0 mins. A trendline is plotted for only the 0 % series for clarity and readability. (b) Table insert displaying the level of removal during the dark period (-20 mins to 0 mins) along with the photocatalytic rate after 10, 20 and 45 mins of irradiation.

It was evident that alongside photocatalytic removal, photolysis, adsorption and homogenous H₂O₂ oxidation (both dark-H₂O₂ and UV-H₂O₂) all played a role in the overall mechanism. As we have previously reported, the degradation of MCPA can be described as '*photocatalytically enhanced*' as the compound will slowly breakdown

under UV irradiation in the absence of a photocatalyst (Kelly et al., 2019). The addition of H_2O_2 in this study further supports this, as under dark and light control conditions, the degradation of MCPA was generally accelerated with increasing H_2O_2 concentration, as highlighted in Figure 2 and further detailed in Table 2. When under photocatalytic conditions, Table 2 (which presents the data as percentage removal of MCPA) confirms the findings shown in Figure 2. In relation to photolysis, the results were expected as under these conditions, the primary mechanism was likely to be driven by homogeneous UV- H_2O_2 oxidation (supported by Figure S4). It can be observed that MCPA degradation was linearly enhanced with both increasing irradiation time and H_2O_2 concentration with a ~3-fold increase in removal noted from 0 to 2 % H_2O_2 after 120 mins.

In comparison to photolysis, under dark conditions several interesting observations can be made in relation to both the effect of H_2O_2 and reaction time, which was also highlighted in Figure 2 (b). At 0 % H_2O_2 , MCPA removal was simply due to adsorption onto the surface of TiO_2 as without the presence of irradiation, there was no photo excitation of the catalyst. This level of removal also remained the same throughout the time frame, suggesting an equilibrium had been reached between MCPA and the TiO_2 surface. Upon the addition of 0.01 % H_2O_2 , a decrease in MCPA removal from ~12 to 7.5 % was noted, which also remained unchanged during the 120 mins time frame. This suggests competitive adsorption was occurring due to the additive (H_2O_2) occupying sites on the TiO_2 surface and restricting MCPA adsorption. In contrast, however, increasing H_2O_2 further, demonstrated that removal was likely a direct result of the oxidative strength of the additive itself (1.8 eV), and was proposed to be degradation

(rather than adsorption) due to TiO_2 surface saturation occurring. With the exception of 0.5 % H_2O_2 , an increase in MCPA removal was noted with increasing H_2O_2 concentration and increasing time from 10 to 120 mins, reaching a peak of 80 % for 2 % H_2O_2 after 120 mins.

H_2O_2 (%)	MCPA Degradation (%)								
	Photocatalysis			Photolysis			Dark control conditions		
	10 min	20 min	45 min	10 min	20 min	120 min	10 min	20 min	120 min
0	75.44	95.65	100	2.40	4.99	30.91	11.9	12	12
0.01	88.53	95.69	100	5.32	10.60	40.67	7.50	7.58	7.58
0.05	88.83	95.69	100	8.84	15.46	41.26	3.76	6.20	19.42
0.1	81.05	92.65	100	12.16	17.89	49.05	10.52	14.84	30.16
0.5	80.35	92.38	100	16.36	30.12	61.86	8.18	12.76	24.11
1	84.13	94.59	100	23.90	33.13	66.62	9.41	19.92	54.21
2	65.71	85.89	100	29.95	41.504	85.87	12.44	24.38	80.09

Table 1. Removal of MCPA (% degradation) as a function of H_2O_2 concentration and after 10, 20, 45 and 120 mins of irradiation under photocatalytic (TiO_2 , H_2O_2 and UV), photolysis (UV and H_2O_2) and dark control conditions (TiO_2 and H_2O_2). Note for '100 %' removal values after 45 mins under photocatalytic conditions, this was calculated in respect of the HPLC limit of detection.

The impact of H_2O_2 on MCPA through photocatalytic and photolytic mechanisms is further reflected by the calculated η_{photon} shown in Table 2. As has been depicted

in previous results, the addition of H_2O_2 resulted in an initial increase in efficiency after 10 mins irradiation, with more comparable values recorded after 45 mins (and complete removal to the limit of detection). An increase in η_{photon} from 20.27 (at 0 % H_2O_2) to a peak η_{photon} of 25.38 was achieved upon the addition of 0.05 % H_2O_2 , while the addition of 2 % resulted in a reduction in η_{photon} to 14.35. In contrast to this the η_{photon} for the reaction under photolysis conditions shows an increase with an increasing loading of H_2O_2 . In the absence of TiO_2 , the reaction is driven by UV- H_2O_2 oxidation reaching a peak η_{photon} of 9.11 at 2 % H_2O_2 after 10 mins irradiation.

H_2O_2 (%)	η_{photon}					
	Photocatalysis (irradiation time, min)			Photolysis (irradiation time, min)		
	10	20	45	10	20	120
0	20.27	12.85	4.48	0.73	0.76	1.57
0.01	24.92	13.46	4.69	1.62	1.61	2.06
0.05	25.38	13.71	4.78	2.69	2.35	2.09
0.1	23.59	13.48	4.85	3.70	2.72	2.49
0.5	21.43	12.32	4.44	4.98	4.58	3.14
1	20.15	11.33	3.99	7.27	5.04	3.38
2	14.35	9.38	3.64	9.11	6.31	4.36

Table 2. Calculated photonic efficiencies (η_{photon}) for MCPA removal under photocatalytic (light, TiO_2 and H_2O_2) and photolysis (light and H_2O_2) conditions after 10, 20, 45 and 120 mins irradiation. The η_{photon} was determined as the ratio between 'MCPA

degradation' and '*photon flux*' (Equation 4). The photon flux was calculated to be 8.19×10^{-7} moles of photon min^{-1} .

3.2 Effect of H_2O_2 CMP formation

While the addition of H_2O_2 did influence the rate of MCPA removal, especially in the early stages, the major impact was found to be on the subsequent formation of CMP. With any photocatalytic water remediation-based system, monitoring the intermediate compounds formed must not be overlooked. In this case, it was important to monitor the formation of CMP from photocatalytic degradation of MCPA as both compounds are undesirable. Figure 3 highlights the impact of introducing H_2O_2 into the system in relation to CMP formation under photocatalytic, photolytic and dark control conditions.

The rate of CMP formation was observed to decrease significantly upon the addition of H_2O_2 , with complete removal also achieved within a shorter irradiation. As reported in our previous work and shown here, CMP reached a peak concentration of $>12 \text{ mg L}^{-1}$ (after 20 mins irradiation) under photocatalytic conditions and 0 % H_2O_2 before being oxidized. Interestingly the addition of 0.01 % H_2O_2 resulted in a significant drop in peak formation from 12.3 to 7.6 mg L^{-1} (38.5 % reduction). This trend was also observed upon the addition of H_2O_2 up to 0.5 %, which reached a reduced max formation of 2.1 mg L^{-1} after 10 mins irradiation (82.9 % reduction). Moreover, this was also accompanied by a reduction in the time required to achieve complete removal (to the limit of the HPLC) from 120 to 90 mins. In addition to this, Figure3 (b) also suggests that

removal was assisted by photolysis with CMP both forming and degrading at H_2O_2 concentrations $>0.05\%$.

Upon increasing H_2O_2 further ($> 0.5 - 2\%$) the rate of CMP formation began to increase again, which was predominantly due to CMP formation in the dark. This was also observed at lower H_2O_2 concentrations and is further highlighted by Figure 3 (c). At 0 or 0.01% H_2O_2 , CMP was not detected, which was an indication that the process was still photocatalytic as while MCPA was bound to the surface of TiO_2 , no bond cleavage had occurred to result in intermediate production. In contrast, at higher H_2O_2 concentrations, CMP was forming which was the result of direct homogeneous H_2O_2 oxidation of MCPA. Interestingly however, formation only reached approx. $1.2 - 1.5\text{ mg L}^{-1}$ for all H_2O_2 concentrations $>0.01\%$, suggesting there may have been multiple processes occurring. For instance, it could be assumed that CMP was no longer formed due to dark- H_2O_2 oxidation not degrading MCPA any further. In contrast however, it is also feasible that an equilibrium may have been reached where the formation rate was equal to the rate of degradation. These findings further emphasize the complexity of the system and highlight the challenge in elucidating the role each plays. Current working is focused on exploring these individual roles further and where possible determining the level of synergy achieved when operating simultaneously.

The observations shown in Figure 3 are also key when considering the entire photocatalytic process with a view towards achieving complete pollutant removal. In relation to full MCPA degradation, a starting concentration of 50 mg L^{-1} was typically removed within 25-30 mins of irradiation. To ensure complete removal of CMP, however, the irradiation period must be extended to at least 120 mins (Figure 3 (a)).

This work shows that the required irradiation time to remove both MCPA and CMP could be reduced by the addition of H_2O_2 . At 0.01 %, 120 mins was still required to achieve complete pollutant removal. At concentrations of 0.1, 0.5, 1 and 2 %, however, the required time was reduced to 90, 90, 45 and 60 mins respectively.

Figure 3: (a) the impact of H_2O_2 on CMP formation under photocatalytic conditions as a function of time, where irradiation was started at 0 mins. (b) the effect of H_2O_2 on CMP formation under photolytic conditions (UV and H_2O_2) and (c) the effect of H_2O_2 on CMP formation under dark control conditions (TiO_2 and H_2O_2). For clear comparison, all y-axis scales remained constant (0 - 14 mg L⁻¹). In all graphs ● is 0 %, ● is 0.01 %, ● is 0.05 %, ● is 0.1 %, ● is 0.5 %, ● is 1 % and ● is 2 %.

3.3 Effect of H₂O₂ on photocatalytic mechanism

It is evident from the data shown that the presence of H₂O₂ impacted the mechanism of MCPA removal and subsequent CMP formation. We previously reported that the formation of CMP from MCPA was found to be a selective reaction that took place primarily at the surface of the catalyst. This reaction was facilitated by the binding of the carboxylic acid group of MCPA with the positively charged surface of TiO₂. This binding resulted in selective scission of the carboxylate moiety by OH radicals, forming CMP in the process. The subsequent removal of CMP was proposed to be a result of random OH radical oxidation. The mechanism was confirmed by altering the pH to further induce or restrict the binding taking place.

In the case of H₂O₂, however, the mechanism clearly changes which is evident from MCPA control experiments and CMP formation. While it could be suggested that the addition of H₂O₂ increases the rate of CMP removal (*via* increased OH radical formation), it is more likely that it does the opposite and restricts its formation. The impact of the additive can be broadly observed under two conditions: what happens up to 0.5 % and what happens beyond 0.5 %. Generally, upon increasing the concentration of H₂O₂, it was observed that the overall mechanism transitioned from being predominantly a surface bound photocatalytic system to a system that was dictated by competitive adsorption and non-photocatalytic processes. Up to 0.5 %, the system can be described as enhanced, as the overall kinetics and procedure are favorable for photocatalytic degradation. Beyond 0.5 % however, the mechanism becomes less

controllable and despite fast rates of MCPA removal, the rate of MCPA degradation is reduced and becomes subject to different mechanisms.

Figure 4 illustrates the proposed mechanism of MCPA degradation and subsequent CMP formation in the presence of low ($\leq 0.5\%$) and high ($> 0.5\%$) concentrations of H_2O_2 . The interaction between any photocatalyst and the 'target' compound in a liquid-phase oxidative driven system can generally occur *via* two processes: directly *via* $h\nu_{\text{B}}^+/\text{OH}^\bullet$ attack at the catalyst surface or indirectly *via* the diffusion of OH radicals into bulk. Based on the data presented here, both mechanisms are likely to be occurring. Generally, as the concentration of H_2O_2 increased, competitive adsorption increased between MCPA and H_2O_2 for sites on the catalyst surface. At lower concentrations ($\leq 0.5\%$), the mechanism was expected to be a combination of both direct and indirect oxidation, which is supported by the concentration of CMP that was formed (Figure 4 (a)). Under photocatalytic conditions when no H_2O_2 was added, a high rate of CMP was generated which was a result of the surface binding between MCPA and TiO_2 . As H_2O_2 began to occupy surface sites, the surface reaction was reduced and as a result a decrease in CMP formation was observed. The intermediate that was detected was likely a result of both the surface reaction and random OH radical attack in bulk. Despite this non-specific mechanism taking place, the rate of MCPA degradation was still maintained at a relatively high level; $\sim 1 \text{ mg L}^{-1} \text{ min}^{-1}$ for $\leq 0.5\%$ H_2O_2 .

At higher concentrations of H_2O_2 ($> 0.5\%$), the surface of TiO_2 was proposed to be completely occupied by peroxide, Figure 4 (b). Despite this however, complete MCPA

removal was still achieved across the concentration range (Figure 2). The removal of MCPA is proposed to have occurred *via* a combination of photocatalysis (OH• diffusion into bulk) along with degradation where H₂O₂ itself was acting as the oxidative species, and direct H₂O₂ photolysis as indicated by the light and dark controls shown in Figure 2, Table 1 and Figure S3-S4. Under these conditions, this mechanism is subject to more sporadic and random attack and as such may generate a range of additional products *via* OH• attack of the aromatic ring of MCPA. While this is currently an area of ongoing research, work by Topalov et al. (2001) has previously reported a proposed mechanism for the photo-oxidation of MCPA. Their study included the generation of CMP and subsequent formation of acetic acid *via* OH radical attack on the aromatic ring. Following this, further attack by OH radicals resulted in complete mineralisation and the generation of CO₂ and H₂O, which is expected during photocatalytic removal of organic pollutants. Topalov and colleagues also suggested the formation of HCl as a final product with the overall stoichiometric reaction being summarised in Equation 4 below.

(a)

(b)

Figure 4: schematic illustration of photocatalytic MCPA degradation and CMP formation under (a) partial competitive absorption and (b) complete competitive absorption conditions.

4. Conclusion

In summary, this report has shown that MCPA degradation was significantly impacted by the addition of H_2O_2 , primarily through the suppressed formation of the intermediate CMP. Upon increasing the level of H_2O_2 , the removal of MCPA became a combination of photocatalysis and direct oxidation with H_2O_2 (under dark and UV conditions). The resulting formation of CMP, however, was significantly reduced due to the suppression of the surface binding between MCPA and TiO_2 , which had previously facilitated the production of the intermediate. The data presented here indicated that an optimum loading of 0.5 % H_2O_2 achieved fast MCPA removal ($\sim 1 \text{ mg L}^{-1} \text{ min}^{-1}$, $\eta_{\text{photon}} = 4.4$) while sufficiently reducing both the concentration of CMP formed (2.1 mg L^{-1}) and the irradiation time required to remove it (90 mins). While this study is paramount to fully understanding the mechanism of photocatalytic degradation taking place, it also provides a platform to further investigate the additional products forming during the reaction to establish a full pathway of degradation.

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Enhanced photocatalytic degradation of 2-methyl-4-chlorophenoxyacetic acid (MCPA) by the addition of H_2O_2

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Highlights

- First report of use of hydrogen peroxide to enhance the photocatalytic decomposition of MCPA.
- H_2O_2 found to inhibit the generation of the degradation by-product CMP
- Complete removal of MCP and CMP achieved within 90 minutes photocatalysis
- Optimum removal of MCPA achieved using loading of 0.5 % H_2O_2 ,

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: