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An investigation of the role of pH in the rapid photocatalytic degradation of MCPA and its primary intermediate by low-power UV LED irradiation

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Abstract

The rapid and efficient removal of pollutants from water is of vital importance. The removal of such compounds is often achieved by adsorption techniques, however the deployment of advanced oxidation processes can present a method for complete degradation. 2-methyl-4-chlorophenoxyacetic acid (MCPA) has been shown to be present in high concentrations in waterways, especially in Northern Ireland. Reported here is the rapid removal of MCPA and its primary degradation intermediate, 4-chloro-2-methylphenol (CMP), in a novel propeller fluidised photo reactor under low-power LED UV irradiation (1.05 W). Under optimum conditions (pH=3.8) MCPA was completely degraded within 30 min and CMP within 90 min of UV exposure with a high reaction rate and photonic efficiency of $9.74 \text{ mol}_{\text{MCPA}} \text{ photon}^{-1} \text{ min}^{-1}$. The mechanism of degradation and contaminant-TiO₂ surface interaction are elucidated through investigation of the impact of pH on photocatalytic activity.

Keywords: Photocatalytic reactor, MCPA, Light Emitting Diodes, Water quality, Degradation mechanism

1. Introduction

Rapid industrial development, intensive agriculture, prolonged drought periods and global population growth have resulted in an ever-increasing demand and shortages for clean water sources. In 2015 it was estimated that 663 million people worldwide did not have access to clean drinking water resources and instead have to use unprotected wells, springs and surface water [1]. The overuse of herbicides has become a primary concern, especially due to the expansion of sectors such as bioenergy, which is focused on increased crop yields. Herbicides can enter drinking water sources through surface or ground water bodies via run-off, spray drift, volatilisation, direct application or by seepage through the soil. 2-methyl-4-chlorophenoxyacetic acid (MCPA) is a selective herbicide used for the removal of many broad-level weeds in grasslands and cereals. In comparison with other herbicides and pesticides, MCPA has a relatively high toxicity (oral LD₅₀ 800 mg kg⁻¹ in rats) [2]. While MCPA can degrade naturally, its half-life is largely dependent on environmental factors, such as soil pH, with a field half-life between 14-31 days. In marine sediments, however, the half-life can be between 80-400 days. Moreover, flooded conditions further increase the time for MCPA to breakdown due to the lack of oxygen in the soil [3,4]. Additionally, MCPA is weakly retained by soil, hence it is capable of migrating easily, meaning that if used close to a water source it is likely to cause contamination [5].

In Northern Ireland, MCPA is commonly found throughout the region in final water source concentrations over above 0.1 µg L⁻¹ [6]. In May 2015, a sample taken from the Killyhevlin area was found to have MCPA concentrations of 0.8 µg L⁻¹, which exceeds the limits set out by the European Drinking Water Directive (EDWD) by 8 times. The primary cause of this spike was a period of heavy rainfall shortly after the application of the herbicide, which resulted in increased run-off into Lough Erne. This spike, along with other recently reported cases, has highlighted the need for the fast and efficient removal of the compound.

Current water treatment technologies, such as adsorption or coagulation, have limitations as they often only concentrate pollutants or simply transfer them to another phase or media, and in doing so, fail to completely remove the threat [7]. Furthermore, additional conventional methods, such as filtration, sedimentation, membrane and chemical technologies, are associated with high operating costs as well as the possibility of generating toxic secondary pollutants [8].

The deployment of advanced oxidation processes (AOPs) for the treatment of water and removal of contaminants has been well documented in the literature [9,10]. Recent publications have also shown that a broad range of AOPs continue to be effective in the treatment of wastewater with examples including cavitation [11], basic pH AOPs [9], photocatalysis [12] and sulfate radical based AOPs [13,14]. Of these however, photocatalysis shows significant potential due to its ability to operate under ambient conditions, its low cost and maintenance, and its non-selective and highly oxidising power [15]. In photocatalysis, the absorption of a photon of sufficient energy by a catalyst results in excitation and subsequently the formation of an electron-hole pair. These charged species then migrate to the catalyst surface where they undergo oxidation and reduction reactions with OH^- and O_2 to form radicals such as $\text{OH}^\cdot$ and $\text{O}_2^{\cdot-}$. While photocatalysis has been deployed across a number of fields since its initial discovery in 1972 [16], its most efficient applications are found in environmental remediation [17]. With continued advancements in the field, there is now increased focus on developing systems that are both energy efficient and have a view towards larger scale deployment. The shift from traditional high-power arc lamps to low power or light emitting diode (LED) alternatives is evident in recent literature [18–22]. The advantages of a LED driven system go beyond the generic benefits of energy and cost efficiency and can include specific wavelength matching to catalyst bandgap to minimise ‘wasted’ photons, versatility and flexibility in geometrical LED arrays to improve light distribution and penetration, and narrow viewing angles to ensure direct irradiation of a specific catalytic area within a reactor.

Despite the photocatalytic removal of MCPA being previously reported in the literature, it remains a significant challenge in water treatment. To date the majority of publications on photocatalytic MCPA

removal have focused on using either bare TiO₂ or doped TiO₂ using boron [23], nitrogen [24], or tungsten [25] as dopants. The removal of MCPA along with three other pesticides *via* LED driven photocatalysis has also previously been reported by Yu *et al.* [26], who showed complete mineralisation under prolonged exposure. Yet to be reported in literature however, is the degradation pathway of MCPA and subsequent removal of the primary intermediate, 4-chloro-2-methylphenol (CMP), under UV-LED irradiation. The formation of CMP should not be overlooked in these studies as its toxicity, while lower than MCPA, is still significant at an oral LD50 1,190 mg kg⁻¹ for rats [27]. Therefore, it is vital to ensure the treatment process can achieve complete degradation of all toxic compounds.

Reported here is the rapid photocatalytic breakdown of the herbicide MCPA, along with the subsequent removal of the reaction intermediate CMP. The breakdown achieved here is not only the fastest reported in the literature to date but also the first publication on the formation and subsequent removal of CMP as the primary intermediate. The investigation was performed in a novel propeller fluidised photo reactor under irradiation from a single UV-LED, which has a low electrical demand of 1.05 W. In addition to observing the formation and removal of reaction intermediates, the impact of pH was studied with a view towards understanding the interaction between MCPA, the catalyst surface and CMP formation.

2. Experimental

2.1 Materials

HPLC grade solvents, 2-methyl-4-chlorophenoxyacetic acid (MCPA), 4-chloro-2-methylphenol (CMP), nitric acid (65%) and NaOH (≥98%, pellets) were purchased from Sigma Aldrich (Gillingham, UK). TiO₂ P25/20 was purchased from Evonik (Milton Keynes, UK).

2.2 Reactor concept

A propeller fluidised photoreactor (PFPR) was used for the photocatalytic experiments performed in this study. Full details on the PFPR can be found in a previous publication [28]. 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 (1.05 W), 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 of 3.5 dcV and I_F of 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. When operating at 1,200 rpm, the propeller created a vortex in the catalyst-herbicide suspension, which allowed for excellent light penetration and distribution within the unit. To ensure maximum light utilisation, a thin layer of aluminium foil was placed around the annular quartz glass body. The reactor system is depicted in Figure 1.

2.3 Photocatalytic procedure

MCPA degradation was performed in the PFPR over P20 TiO₂ 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 supplementary information) 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. During dark only conditions, MCPA and CMP concentrations were monitored, with any drop being a result of binding to the catalyst surface. 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 of the system, the photon flux was determined using the potassium ferrioxalate actinometrical method [29,30]. The LED irradiance was also determined at two points within the reactor; at the top of the reaction mixture during mixing (12.15 mW cm^{-2}) and at the base of the unit where the propeller was located (1.55 mW cm^{-2}). 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 using the following equation.

$$\text{Equation 1} \quad \text{Photonic efficiency (mol photon}^{-1}\text{)} = \frac{\text{Reaction rate (mole min}^{-1}\text{)}}{\text{Photon flux (Einsteins L}^{-1}\text{min}^{-1}\text{)}}$$

The influence of pH to the photocatalytic degradation was studied in the range of $2 \leq \text{pH} \leq 10$. The pH of a 50 mg L^{-1} MCPA solution was 3.8. This was adjusted with HNO_3 to $\text{pH}=2$ and $\text{pH}=3$, and with NaOH to $\text{pH}=4$, $\text{pH}=6$, $\text{pH}=8$ and $\text{pH}=10$. All experiments were performed in duplicate throughout the investigation. All data shown herein are based on calculated mean values with standard deviation also determined.

2.4 Determination of MCPA and CMP by HPLC

The concentration of MCPA and CMP in the collected samples was determined by HPLC, using an Agilent 1100 HPLC system, equipped with a fluorescence detector (FLD) recording traces at 230 nm excitation (Ex.) - 320 nm emission (Em.). A Phenomenex KinetexTM phenyl-hexyl analytical column ($150\text{mm} \times 4.6\text{mm}$, $5\mu\text{m}$) was used, thermostated at 40°C , and the mobile phase was 60:40 methanol/water containing 0.1% acetic acid. The flow-rate was 1 mL min^{-1} and the injection volume was $5 \mu\text{L}$. Under these conditions MCPA elutes at 5.3 min and CMP at 4.1 min. The LOD of the developed method was 0.033 mg L^{-1} and the LOQ was 0.1 mg L^{-1} for both analytes.

3. Results and Discussion

The photocatalytic removal of MCPA *via* a rapid and energy efficient pathway is paramount to the further development and potential deployment of this technology. Moreover, it is crucial to fully understand the

mechanistic degradation pathway to ensure complete removal of all toxic compounds. In view of this, the following results and discussion focus not only on full MCPA breakdown, but also the formation and subsequent degradation of the primary intermediate CMP under a single high intensity low power UV LED. The impact of pH on degradation reveals the likely mechanism taking place and the relationship between surface bound reactions and the target solutes.

3.1 Photocatalytic degradation of MCPA

MCPA is an ideal target for photocatalytic removal due to its high solubility in water and its strong electrostatic attraction to TiO_2 . The combination of its acidity ($\text{pK}_a=3.73$) and the isoelectric point of TiO_2 ($\text{pI}=6.2$), ensure strong binding at the surface of the photocatalyst, which facilitates the breakdown. In any heterogeneous catalytic reaction, the initial adsorption of target molecules to the surface is crucial to ensuring a high efficiency of the desired reaction. As a result, the removal of MCPA under photocatalytic conditions as shown in Figure 2 was rapid with complete degradation of a 50 mg L^{-1} starting concentration within 30 minutes of UV exposure. While in the absence of irradiation (dark control conditions) minimal MCPA removal was recorded (with no detectable CMP formation), exposing MCPA to UV light in the absence of a catalyst (light control conditions) showed both degradation and CMP production. After 120 min of irradiation of a 50 mg L^{-1} MCPA solution, 31% removal was observed, while a final concentration of 6.8 mg L^{-1} of CMP also measured, Figure 2. The rate of conversion and degradation under light control conditions (no catalyst) was significantly slower than under pure photocatalytic conditions, however as the reaction was clearly still proceeding, it suggested that it was '*photocatalytically enhanced*' rather than being purely photocatalytic. Moreover, this highlights the need for rapid removal technologies, as natural MCPA degradation is a lengthy process and will be further prolonged by CMP breakdown.

CMP was detected in the first sample after 5 min of irradiation and reached a maximum concentration of 12.32 mg L^{-1} after 20 min. Thereafter, CMP was broken down at an increasing rate, as MCPA was completely removed and competition for radicals, such as $\text{OH}^\cdot$, diminished. A range of additional

intermediate products were detected, however these were rapidly formed and degraded, and therefore appeared more sporadically in samples. The concentrations at which these intermediates were produced were also far lower than CMP, hence full identification of these compounds utilising HPLC-MS is currently ongoing.

The degradation rates of MCPA shown here appears to be the highest reported in the literature to date, especially if the power consumption and catalyst loadings are taken into consideration. Comparisons between photocatalytic systems in the literature can often be challenging due to a number of varying parameters such as initial starting concentration of pollutant and catalyst, reactor design and operation, irradiation source power and general characteristics. Comparisons drawn here were based on the calculated rate of degradation, denoted as R_{deg} , which was formulated from Equation 2. In addition, R_{deg} was also calculated in relation to 1 g of photo-active TiO_2 material being present, which is a commonly reported unit in the literature.

$$\text{Equation 2} \quad R_{deg} (mg L^{-1} min^{-1}) = \frac{(C_0 - C_1)}{t}$$

Where, C_0 is the initial concentration, C_1 is the final concentration and t is the irradiation time.

In this study, a R_{deg} of $1.60 \text{ mg L}^{-1} \text{ min}^{-1}$ was achieved, while the photonic efficiency removal rate of MCPA moles per photon of irradiation was $9.74 \text{ mol}_{MCPA} \text{ photon}^{-1} \text{ min}^{-1}$. A comparison to the literature based on the calculated R_{deg} is shown in Table 1. A rapid rate of MCPA removal was previously reported by Rivas *et al.* [31] who showed complete breakdown within a 15 min irradiation time. While the overall removal was faster than reported here, a lower starting concentration (5.01 mg L^{-1}) was used along with a significantly higher power irradiation source (60 W), resulting in $R_{deg}=0.34 \text{ mg L}^{-1} \text{ min}^{-1}$. A similar starting concentration of 50 mg L^{-1} was reported by Diaz *et al.* [32], who also achieved complete breakdown after 180 min giving a $R_{deg}=0.28 \text{ mg L}^{-1}$. While a low catalyst loading of 0.2 g L^{-1} was reported in this study, an irradiation source of significantly higher power (150 W) was also used. As Table 1 shows, the R_{deg} normalised by catalyst loadings gives a $R_{deg}=1.39 \text{ mg L}^{-1} \text{ min}^{-1} \text{ g}_{TiO_2}^{-1}$ for the Diaz *et al.* study. In contrast to this, the results presented here provide a $R_{deg} = 3.20 \text{ mg L}^{-1} \text{ min}^{-1} \text{ g}_{TiO_2}^{-1}$. As is

evident from Table 1, the R_{deg} values in this study are significantly higher than that previously reported. When taking into consideration the amount of active photocatalyst material used, the R_{deg} for this investigation was an increase of 130 % over the previous faster R_{deg} [32]. Table 1 also highlights the difference in power of light sources used between this investigation and those previously published in the literature. The LED operated at 1.05 W which is significantly lower than anything previously used for photocatalysis in conjunction with MCPA. To ensure photocatalysis remains as a lower power alternative to more traditional water treatment methods, it is paramount that energy efficient lamps such as LEDs are used.

The rapid breakdown shown in Figure 2 is thought to be primarily due to the ability of the PFPR to both eliminate mass transfer limitations and create excellent light penetration and distribution within the unit [28]. As the LED was positioned directly above the reactor and irradiated into the vortex created, light could reach the catalyst surface without needing to be transmitted through any glass or optical material. Furthermore, a thin aluminium foil lining on the outside of the PFPR ensured minimum to no loss of scattered light.

3.2 Effect of pH

In order to better understand both the mechanism of MCPA removal and the formation of CMP, the effect of pH was studied over the range of $2 \leq \text{pH} \leq 10$. The rate of MCPA degradation is reflected by the time taken to reach 50% and 90% removal of the pollutant, as shown in Figure 3. Generally, in an acidic environment ($\text{pH} \leq 3.8$), an increased rate of removal was observed, with complete breakdown recorded within 45 min for all samples. Under these conditions a $R_{deg} = 1.78 \text{ mg L}^{-1} \text{ min}^{-1}$ was achieved at $\text{pH}=3$. At $\text{pH}=4$, the rate decreased ($R_{deg} = 0.61 \text{ mg L}^{-1} \text{ min}^{-1}$) with complete removal recorded at 75 min, while at $\text{pH}=6$ and $\text{pH}=8$ comparable rates of removal were recorded, achieving complete breakdown in up to 90 min. Only at $\text{pH}=10$, where MCPA was likely electrostatically repelled from the TiO_2 surface, was complete removal not achieved within the 120 min irradiation period (Figure 3-insert).

Figure 4 shows the impact of pH on CMP formation in relation to the concentration of the intermediate formed and the time taken to reach the max concentration before photocatalytic degradation began. The production of CMP generally followed the profile of MCPA removal with rapid degradation leading to CMP peak increase especially in the range of $2 \leq \text{pH} \leq 4$. Under these acidic conditions, both the peak production and conversion percentage increased significantly. At a pH=2, a peak production of 18.7 mg L^{-1} was achieved after only 25 min of irradiation, which equated to 53.5 % conversion from MCPA. With increasing pH, a decrease in CMP formation was observed with the lowest recorded value being 2.8 mg L^{-1} (16.5 % conversion), after 30 min UV irradiation at pH=10. Interestingly, at pH=2 a reduced rate of CMP removal was observed when compared to all other conditions. This reduced activity of the photocatalytic reactor is attributed to a diminished amount of $\text{OH}^\bullet$ radicals. At pH=2, the excess H^+ present acts as strong electron scavenger, producing $\text{H}^\bullet$, which compete with CMP for $\text{OH}^\bullet$ radicals. As CMP has a low affinity for TiO_2 (see following section) it is likely $\text{OH}^\bullet$ and $\text{H}^\bullet$ radicals would combine to form H_2O (Equations 3-4), thus reducing the number of non-surface bound radicals available for CMP degradation.

The impact of pH on the photonic efficiency of MCPA degradation, CMP formation and subsequent degradation is shown in Table 2. The results confirmed that in acidic environment the efficiencies are enhanced for both pollutant removal and intermediate formation. Furthermore, the photonic efficiency for CMP degradation of $0.88 \text{ mol}_{\text{CMP}} \text{ photon}^{-1}$ agrees with the above observation regarding the slow removal rate of CMP at pH=2. At pH=3, the photonic efficiency of CMP formation was significantly higher at $8.61 \text{ mol}_{\text{CMP}} \text{ photon}^{-1}$, which was a result of the rapid rate of production (15.09 mg L^{-1}) after only 15 min irradiation. This also lead to the highest CMP degradation efficiency at $1.08 \text{ mol}_{\text{CMP}} \text{ photon}^{-1}$. Interestingly, at pH=3.8 a similar CMP degradation efficiency was recorded ($1.03 \text{ mol}_{\text{CMP}} \text{ photon}^{-1}$), while maintaining a much lower formation efficiency of $5.13 \text{ mol}_{\text{CMP}} \text{ photon}^{-1}$. This observation, coupled with

the high rate of MCPA degradation ($9.74 \text{ mol}_{\text{MCPA}} \text{ photon}^{-1}$), confirmed that using an unmodified pH presents the optimum conditions for maximum pollutant destruction.

3.3 Degradation mechanism

One of the main observations from the above data was the rapid appearance of CMP, which gave a clear indication as to the mechanism of breakdown. To investigate this further, experiments were performed under a narrower irradiation time frame with samples collected in shorter intervals (see supplementary information). The data shows breakdown of MCPA and conversion to CMP started within the first 10 s of irradiation and was likely initiated as soon as the LED was switched on. As CMP was not detected during any dark periods of the reaction, it is proposed that its formation is a result of photon-induced $\text{OH}^\cdot$ radical cleavage.

As discussed above, the unadjusted pH of MCPA solutions, coupled with the isoelectric point of TiO_2 facilitate strong adsorption of the pollutant on the catalyst surface. This is demonstrated in Figure 5, which depicts the amount of MCPA and CMP bound by the catalyst at each studied pH. Thus, maximum MCPA binding is observed at $3 \leq \text{pH} \leq 3.8$, while as expected by its molecular structure, CMP has significantly weaker affinity for the catalyst with only marginal binding at $4 \leq \text{pH} \leq 8$. Furthermore, the data also suggests that at $\text{pH}=10$ there was virtually no MCPA adsorption onto the catalyst surface, implying that under these conditions, photocatalytic activity was dictated by the rate of $\text{OH}^\cdot$ radical diffusion and the reactor ability to eliminate mass transfer limitations. Interestingly, a strong correlation of the amount of MCPA bound to the surface of the catalyst at equilibrium and its half-life was found (Figure 5-insert), further confirming the process is driven by the surface bound reaction.

The formation of CMP in as few as 10 s of UV irradiation, suggests it was the carboxylic acid moiety of MCPA that was tethered to the surface of the catalyst. Therefore, upon UV irradiation and generation of $\text{OH}^\cdot$ radicals, this bond was cleaved releasing CMP from the surface of TiO_2 . This observation is supported by previous findings reported in literature, whereby the binding of MCPA to TiO_2 was

confirmed to be *via* the electronegative carboxylate group, as illustrated by a Hyperchem-derived molecular electrostatic (HME) potential model [24]. The final degradation of CMP, which was not confined to the surface of the catalyst to any appreciable extent, is thought to be a combination of both surface reactions and $\text{OH}^\cdot$ radical diffusion in bulk. To support this, the effect of pH on CMP degradation was also investigated (Figure 6). Here, based on the maximum observed concentration of CMP, 30 mg L^{-1} solutions of varying pH values in the range $2 \leq \text{pH} \leq 10$ were irradiated under the same conditions as described above. The data suggests that pH had no significant impact on the degradation of CMP, with the exception of $\text{pH}=2$ and $\text{pH}=10$, whereby the excess H^+ and OH^- ions respectively, result in reduced availability of $\text{OH}^\cdot$ radicals [33].

Based on the above observations, the overall mechanism of MCPA removal and subsequent CMP formation as demonstrated in this study, can be summarised as follows: the catalyst adsorbs a significant amount of MCPA at moderately acidic pH values, which results in rapid photodegradation of the pollutant and formation of CMP within seconds of exposure to UV light. CMP is released to the bulk of the reactor, and thanks to efficient mixing within the vessel, is eventually degraded by $\text{OH}^\cdot$ radicals diffusing from the surface of the catalyst (Figure 7).

4. Conclusions

In this manuscript, we present the application of a novel fluidised propeller photocatalytic reactor in the removal of MCPA and its main degradation product, CMP in distilled water. Our design utilised a single 1.05 W UV LED and was able to achieve a $R_{\text{deg}} = 1.60 \text{ mg L}^{-1} \text{ min}^{-1}$ for MCPA and a photonic efficiency of $9.74 \text{ mol}_{\text{MCPA}} \text{ photon}^{-1} \text{ min}^{-1}$, which are the highest values reported to date in literature. The impact of pH was investigated as a means to elucidate the mechanism of degradation. In highly acidic conditions ($2 \leq \text{pH} \leq 4$), rapid MCPA removal coupled with significant CMP formation highlights the significance of the interaction between the pollutant and surface of the catalyst. The binding of the carboxylic group of MCPA to TiO_2 resulted in the cleavage of the bond by $\text{OH}^\cdot$ radicals and subsequently in the rapid

formation of CMP. The degradation of CMP was likely due to a combination of continued interaction with the TiO_2 surface and $\text{OH}^\cdot$ radicals which had diffused in the bulk of the reactor. This is the first time the mechanism of MCPA conversion to CMP has been investigated via a surface bound reaction and the first report on the photocatalytic degradation of MCPA and CMP. In the case of $\text{pH}=2$, competition for $\text{OH}^\cdot$ between CMP and $\text{H}^\cdot$ lead to a slow rate of pollutant degradation. Under basic conditions, lower levels of binding of MCPA on the TiO_2 surface were observed, due to electrostatic repulsion, and as such CMP formation was also reduced. These key results provide an excellent platform to further develop photocatalytic technology with a view towards deployment for waste water treatment.

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Figure Captions

Figure 1(a) Schematic representation of the PFPR with UV-LED positioned above where (1) is the bilge pump motor and SS 316 bottom flange, (2) is the SS 316 propeller, (3) is the annular quartz body, (4) is the SS316 top flange and (5) is the 370 nm LED mounted onto a heatsink; (b) Image of PFPR in operation.

Figure 2 Photocatalytic degradation of MCPA and subsequent formation and degradation of CMP as a function of irradiation time at pH=3.8. Control experiments were performed in the absence of light for MCPA and CMP and in the absence of a catalyst for MCPA and CMP. The MCPA solution was given 20 min in the dark to equilibrate with irradiation being switched on at 0 min.

Figure 3 The effect of pH on the photocatalytic degradation of MCPA as represented by the time taken to achieve 50% and 90% destruction. Insert: Removal of MCPA as a function of irradiation time.

Figure 4 The impact of pH on CMP formation in relation to max concentration, [CMP]_{max} (left axis, bar chart), final concentration, [CMP]_{final} (left axis, bar chart) and the time taken to reach [CMP]_{max} (right axis, line graph). [CMP]_{final} was taken as the concentration remaining after 120 mins of UV irradiation.

Figure 5 Effect of pH on the quantity of pollutant absorbed onto the of the catalyst in the dark. The starting concentration was 50 mg L⁻¹ and 30 mg L⁻¹ for MCPA and CMP respectively, while the loading of TiO₂ P20 was 0.5 g L⁻¹. Insert: Correlation of amount of MCPA bound on the catalyst and its half-life.

Figure 6 The effect of pH on the photocatalytic degradation of CMP (30 mg L⁻¹) at different pH values.

Figure 7 Photocatalytic schematic diagram for proposed degradation pathway of MCPA and CMP under acidic conditions.

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Table 1 Comparison of MCPA degradation rates (R_{deg}), starting concentration, catalyst loading and light source power

Paper	MCPA starting concentration (mg L^{-1})	Catalyst loading (g L^{-1})	Light source power (W)	R_{deg} ($\text{mg L}^{-1} \text{min}^{-1}$)	R_{deg} per g of TiO_2 ($\text{mg L}^{-1} \text{min}^{-1} \text{g}_{\text{TiO}_2}^{-1}$)
Presented work	50.00	TiO_2 P25/P20 -0.5	1.05	1.6	3.20
Rivas <i>et al.</i> [27]	5.01	TiO_2 P25 - 0.5	60	0.34	0.68
Diaz <i>et al.</i> [28]	50	TiO_2 P25 -0.2	150	0.28	1.39
Abramović <i>et al.</i> [20]	200	TiO_2 P25 - 2	125	2	1
Zertal <i>et al.</i> [30]	112	TiO_2 P25 - 1	125	0.75	0.75
Mendiola-Alvarez <i>et al.</i> [31]	10	TiO_2 P25 - 1	800 W/m^2	0.08	0.08

Table 2 Calculated photonic efficiency values ($\text{mol}_{\text{pollutant}} \text{photon}^{-1}$) for the degradation of MCPA, formation of CMP and subsequent degradation of CMP.

pH	MCPA	CMP	
	Degradation	Formation	Degradation
2	6.30	6.41	0.88
3	10.81	8.61	1.08
3.8	9.74	5.13	1.03
4	3.73	2.79	0.56
6	3.34	1.55	0.34
8	3.34	1.30	0.40
10	2.38	0.79	0.14

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Highlights:

- Rapid degradation of MCPA achieved using a low power LED photocatalytic system
- pH impact on MCPA degradation, CMP formation and subsequent degradation is presented
- Degradation is accelerated at acidic pH, facilitated by MCPA binding to the TiO₂ surface
- The degradation of CMP has an optimal pH range = 2 > pH < 10, which facilitates efficient reaction between the compound and OH•