

**Photocatalytic degradation of microcystin-LR by modified high-energy {001} titanium dioxide: Kinetics and mechanism study of HF8**

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Research

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**ABSTRACT***Background:*

Uniquely synthesised titanium dioxide (TiO<sub>2</sub>) with high-energy {001} exposed facets denoted HF8 was used for the photocatalytic degradation of microcystin-LR (MC-LR) under ultraviolet irradiation at 365 nm.

*Methods:*

The influence of various conditions including environmental pH, nutrient anions, TiO<sub>2</sub> dose, and MC-LR concentration was studied, and concentration of MC-LR measured using liquid chromatography-tandem mass spectrometry.

*Results:*

Within 120 min, 72.6% of an environmentally rele-

vant MC-LR concentration (120 µg/L) was degraded under pH conditions ranging from 3 to 11. Stability tests revealed no loss of TiO<sub>2</sub> activity after four applications of the same dose, indicating its stability, reusability, and potential to be re-used for sustainable remediation of MC-LR in eutrophic waters. Mechanism studies suggested that the reaction obeyed the pseudo-first-order equation and that hydroxyl radicals are the major reactive intermediate contributing to the reaction. The structure elucidation of intermediates suggested that hydroxylation and bond cleavage between the Adda chain and Mdha site could be the initiation of reactions in the degradation of MC-LR by HF8 TiO<sub>2</sub>.

*Conclusion:*

The results present a fast, sustainable, and practical

method using modified TiO<sub>2</sub> to improve MC-LR remediation.

**Keywords:** Degradation, Microcystin-LR, Photocatalysis, Titanium dioxide

## 1. INTRODUCTION

Cyanobacteria are ubiquitous, and nowadays blooms are occurring more frequently in surface waters due to numerous factors, especially anthropogenic pollution [1]. Microcystins (MCs), reportedly the most common cyanobacterial toxins, are potent hepatotoxins and tumour promoters and therefore, pose not only a risk to human health but also the environment as a whole [2]. Humans can be exposed to cyanobacterial toxins via several routes including potable water, recreational activities, and the food chain [3-5]. To date, more than 100 analogues of MCs have been identified [6]; among them, microcystin-LR (MC-LR) is the most frequently occurring MC and reported to be the most harmful [7]. Therefore, a guideline value of 1.0 µg/L MC-LR in drinking water and a tolerable daily intake (TDI) of 0.04 µg MC-LR/kg body weight per day in aquatic products were proposed by the World Health Organization (WHO) [8,9].

MCs are very stable in the environment and remain toxic in natural waters for months, even years, plausibly since they can resist high temperatures (up to 40°C), extreme pH values, sunlight, and enzymes [10,11]. Thus, MCs are resistant to most of the conventional physical and biological technologies currently known. Advanced oxidation processes could be effective for MC elimination in the presence of strong oxidants, such as chlorine, ozone, and hydrogen peroxide [12,13], though the continuous input of expensive chemical reagents is not only futile but prohibited. Recently, a photocatalysis technology using a combination of UV radiation together with titanium dioxide (TiO<sub>2</sub>) was proven as a good strategy for the removal of organic pollutants in wastewaters. This system exhibited fast, effective, and environment-friendly properties in the mineralisation of pollutants by producing strongly oxidative electron/hole pairs, i.e., H<sup>+</sup>, O<sub>2</sub><sup>-</sup>, and <sup>•</sup>OH radicals [14-16]. Several aspects of TiO<sub>2</sub>, such as the crystalline phase, crystal-

linity, particle size, surface area, specific surfaces, and growth orientation of TiO<sub>2</sub> nanocrystals, have been studied [17-19]. Different surface energy levels of the conduction and valence bands drive the electrons and holes to different crystal faces, which leads to the separation of electrons and holes, thereby enhancing the photocatalytic activity [17,20]. Most available anatase TiO<sub>2</sub> crystals are dominated by the thermodynamically stable {101} facets, rather than the {001} and {010} facets which are a great deal more reactive [18,21]. Therefore it was deemed necessary to create and test TiO<sub>2</sub> crystals with more reactive facets in order to advance MC-LR remediation in wastewater treatment plants.

In the present study, anatase TiO<sub>2</sub> nanocrystals with exposed high-energy {001} facets (denoted HF8) were investigated for their MC-LR degradation potential. The aims of the study were to monitor the course of the process (degradation rate, intermediate products) of MC-LR degradation and to assess the effects of various experimental parameters, such as catalyst loading, initial and substrate concentration, pH, and re-usability, with regard to evaluating HF8's practical applicability in nature and water treatment plants as well as the future development of a robust standardized testing regime for photocatalytic performance toward water purification.

## 2. MATERIALS AND METHODS

### 2.1. Chemicals

All chemicals were analytical grade and purchased from Sigma-Aldrich unless stated otherwise. MC-LR (95% purity) was purchased from Enzo Life Sciences, Alexis Biochemicals, (Lörrach, Germany).

The modified {001} facet and thus a more reactive TiO<sub>2</sub> was prepared by Professor Kangle Lv (South-Central University of Nationalities, China); briefly, 8 mL of hydrofluoric acid (HF) were added dropwise to 50 g of tetrabutyl titanate while stirring. The resulting solution was then transferred to a dried 100 mL Teflon-lined autoclave and kept at 200°C for 24 h. After being cooled to room temperature, the precipitates were filtrated through a membrane filter (pore size, 0.45 µm), and thoroughly rinsed with distilled water until the pH value of the filtrate is 7 ± 0.2. Then the

precipitates were dried in a vacuum oven at 80°C for 10 h. The resulting sample was denoted as HF8 [22].

## 2.2. Factors affecting MC-LR degradation by HF8

### *i. Concentration of MC-LR*

MC-LR, at concentrations ranging from 5 to 120 µg/L, was mixed with 500 mg/L HF8 TiO<sub>2</sub> and stirred at 20°C for 60 min in the dark to achieve adsorption equilibration. Thereafter, an LED lamp (the wavelength centred mainly at 365 ± 10 nm) was switched on to initiate the photocatalytic reaction while continually stirring. During irradiation, 1.0 mL of the reaction suspension was withdrawn at given intervals (i.e. after 30 s, 1 min, 5 min, 10 min, 30 min, 60 min, and 120 min) and centrifuged to remove the HF8 particles at 10,000 × g for 10 min before liquid chromatography-tandem mass spectrometry (LC-MS/MS) analysis. Two controls were simultaneously conducted; namely, 1) 120 µg/L MC-LR in the absence of the catalyst and irradiation to assess the natural degradation of MC-LR under the experimental conditions; and 2) 120 µg/L MC-LR together with TiO<sub>2</sub> precipitate without the addition of HF (HF0). All the experiments were conducted in triplicate.

### *ii. Concentration of the photocatalyst HF8*

The experiment in section 2 b i) was repeated exactly as detailed above, however, with the exception that the MC-LR concentration was kept constant at 100 µg/L and the HF8 concentration was varied (50, 100, 200, 500, and 1000 mg/L). All reactions were conducted in triplicate.

### *iii. pH-range and nutrient anions*

The effect of pH was observed by adjusting the pH of the reaction media with 0.1 M HCl and NaOH solutions to pH 3, 5, 7, and 11 before the start of the reaction as detailed above, in triplicate.

The concentrations of total nitrogen and total phosphate were set at 2000 and 100 µg/L by adding NaNO<sub>3</sub> and KH<sub>2</sub>PO<sub>4</sub> respectively, before the start of the reaction (in triplicate). These selected concentrations were based on data from the Class IV of the ECE standard statistical classification of surface freshwater quality for the maintenance of aquatic life [23] to assess the effect of eutrophication and to rep-

resent the scenario in nature.

### *iv. Recycling and reusability*

After stirring in the dark for 60 min to ensure adsorption equilibrium, 500 mg/L HF8 was used to degrade 20 µg/L MC-LR for 24 h. Then, the HF8 was separated by centrifugation at 10,000 × g for 10 min and added to a second 20 µg/L MC-LR solution for adsorption and photocatalysis; this was repeated for four cycles, always using the same catalyst mixture from the previous reaction, completely unmodified. The reusability test was conducted in triplicate.

### *v. Roles of reactive oxygen scavengers*

The series of tests were conducted as detailed above, however, with the addition of scavengers to study the mechanism responsible for the photocatalysis of HF8. Sacrificial agents including ammonium oxalate (AO), tert-butanol (TBA), and benzoquinone (BQ), were added to the degradation system to ascertain the active species, i.e. H<sup>+</sup>, ·OH, and O<sub>2</sub><sup>•-</sup>, respectively responsible for the degradation process. The dosage for the scavengers were 0.1 mmol/L AO, 20% TBA, 10 mmol/L BQ [24-26].

## 2.3. Quantitative analysis of MC-LR

All analyses were conducted on an Agilent 1200 infinity series liquid chromatographer coupled to an Agilent 6460 triple quadrupole mass spectrometer (LC-MS/MS) with electrospray ionisation (AJS-ESI). Chromatographic separation was achieved on a Kinetex reverse phase C18 (1.7 U, 100 Å, 50 × 2.1 mm) column (Phenomenex) maintained at 40°C and the sample injection volume was 10 µL. The mobile phase consists of 0.1% formic acid aqueous solution in MS grade water (solvent A) and 0.1% formic acid in MS grade acetonitrile (solvent B). The linear elution gradient was started at 5% ACN, which was ramped to 95% over the course of 6 min and held constant for 3 min before returning to the original conditions to re-equilibrate the column for 3 min. The flow rate was maintained at 0.4 mL/min during analysis. The LC conditions resulted in an elution time of 7.7 min for MC-LR. For MC/MS verification, the drying gas temperature and flow rate were set at 320°C and 8 L/min, and the sheath gas temperature and

flow rate were set at 380°C and 11 L/min. The capillary voltage was set to 5 kV. The instrument was operated in a positive ion mode. MC-LR were monitored by multiple reaction monitoring (MRM) mode ( $m/z$  995.5 to 155, 135, and 213), using a fragmentor voltage of 180 V, and collision energies of 80, 86, and 75 V for each respective fragment.

#### 2.4. Qualitative elucidation of the MC-LR breakdown products

To assess the MC-LR degradation products, a 100 µg/L MC-LR solution was treated with 500 mg/L HF8, as before, for 10 min, 30 min, 60 min, and 120 min under UV irradiation (3 W/m), in triplicate. The treated MC-LR solution was first purified by centrifugation (10,000 × g, 10 min). For comparison purposes, the MC-LR solution was also analysed before treatment. The purified samples were analysed using the same system as stated before and using the same chromatographic settings, however, with tandem mass spectrometry in full scan mode.

#### 2.5. Kinetic analysis

The Langmuir-Hinshelwood equation, which is often used to model the photocatalytic oxidation kinetics of many organic compounds, was used as expressed in Eq. [1]:

$$r = -\frac{dC}{dt} = \frac{k_r KC}{1+KC} \quad [1]$$

Where  $r$  is the reaction rate (µg/(L min)),  $C$  is the concentration of the targeted pollutant at time  $t$  (mg/L),  $t$  is the irradiation time (min),  $k_r$  is the reaction rate constant (1/min), and  $K$  is the adsorption coefficient of targeted pollutant on a photocatalyst particle (L/µg). Since  $KC$  is usually less than 1.0, the presence of  $KC$  as the denominator is negligible and integrated with time  $t$ . Therefore, Eq. [1] was simplified to a pseudo-first-order kinetic equation [27,28] as described below in Eq. [2].

$$\ln \frac{C_0}{C} = k_r K t = k_{app} t \quad [2]$$

Where  $C_0$  is the initial concentration of the targeted pollutant (mg/L). The apparent reaction rate constants ( $k_{app}$ ) for the photocatalytic degradation of targeted

pollutant were evaluated from experimental data using linear regression analysis.

#### 2.6 Data treatment

Agilent native MassHunter® data files were converted to .cdf data using Xconvert program and following this the data were imported to MZmine 2.21 and processed applying the baseline correction, peak detection, deconvolution, deisotoping, alignment, and gap-filling procedures.

Statistical analysis was performed using Statistical Package for Social Sciences (SPSS) software (version 21, SPSS, Inc, Chicago, IL, USA;  $\alpha = 0.05$ , 95% CI). Data were tested for normality and homogeneity of variance using Shapiro-Wilk test and Levene's test, respectively. A one-way analysis of variance test was performed followed by a Turkey's post-hoc-test to identify significant differences between data points ( $\alpha = 0.05$ ).

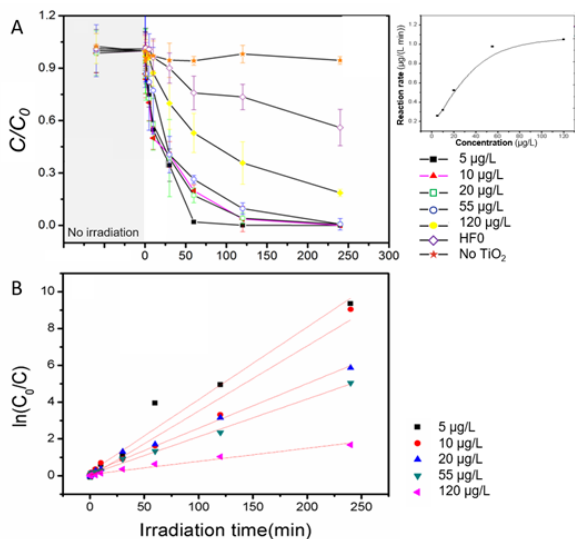
### 3. RESULTS AND DISCUSSION

#### 3.1. Effect of initial MC-LR concentration

Figure 1A presents the degradation of MC-LR starting with different initial concentrations using the photocatalytic activity of HF8.  $C/C_0$  represents the ratio between the concentration measured at each time point and the initial concentration. Compared to the degradation process without the addition of the catalyst, HF8 significantly improved MC-LR degradation ( $p < 0.05$ ). With an initial MC-LR concentration of 5 µg/L, on average 72.6% more MC-LR was degraded within 60 min, and the reaction can be completed after 120 min. Starting with 120 µg MC-LR/L up to 48% more MC-LR could be degraded compared to the reaction occurring in the absence of HF8. This indicates that the catalyst is active and effective for MC-LR degradation within the investigated concentrations ranging from 5 to 120 µg/L.

According to Eq. [2], the influence of the initial concentration of MC-LR on the photocatalytic degradation rate is shown in the inset of Figure 1A. The rate of degradation increased from 0.26 to 1.07 µg/(L min) with an increase in the initial MC-LR concentration from 5 to 120 µg/L, however, the reaction rate plateaued with the higher initial concentrations, i.e.

MC-LR concentrations above 60  $\mu\text{g/L}$ .

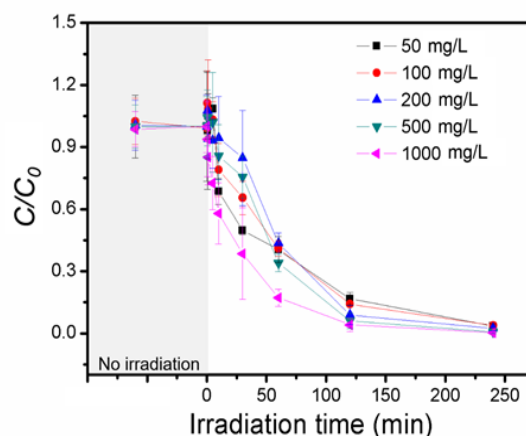


**Figure 1.** (A) Photocatalytic activity of HF8 for MC-LR degradation as a function of irradiation time, obtained at different MC-LR initial concentrations. Data represent the average ratio of the MC-LR concentration per time point to initial concentration  $\pm$  standard deviation ( $n = 3$ ). Insert: Variation of the initial rate of MC-LR degradation versus different initial concentrations. (B) The linear variation of  $\ln(C_0/C)$  versus irradiation time for MC-LR with different initial concentrations.

A plot of  $\ln(C_0/C)$  versus  $t$  for all the experiments with different initial concentration is shown in Figure 1B. The degradation process fits the pseudo-first-order kinetic equation with  $r^2$  values ranging from 0.969 to 0.995 under the investigated concentrations. The values of  $k_{app}$  can be obtained directly from the regression analysis of the linear curve in the plot. The  $k_{app}$  decreased from 0.064 to 0.009 with increasing initial MC-LR concentrations. This result can be explained by the limitation of active centres on the photocatalyst. In other words, with the addition of excessive MC-LR, the active centre of the catalyst was mostly occupied (by the MC-LR and/or the produced intermediates), thereby reducing the solar light adsorption capability and leading to decreased reaction rate [29]. Therefore, the effect of the photocatalyst concentration was investigated to overcome this limitation.

### 3.2. Effect of HF8 concentration

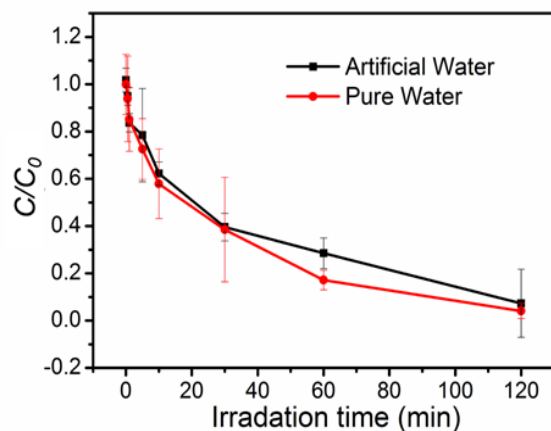
Previously, it was reported that photocatalysis is a catalyst mass dependent reaction. A larger catalyst mass can produce more hydroxyl radicals and/or electrons by absorbing more photons; however, excessive catalyst mass will reduce the opacity of suspension, blocking the energy from light radiation, thereby decreasing the degradation efficiency [29]. To optimise the catalyst mass, five different catalyst concentrations, namely 50, 100, 200, 500, and 1000 mg/L HF8, were used for this investigation. In Figure 2, which shows the influence of catalyst concentration on the photocatalytic degradation activity of 100  $\mu\text{g/L}$  MC-LR, it is evident that for the first 10 min of the reaction, the concentration of the HF8 was negligible ( $p > 0.05$ ), however, after 30 min using 200 mg/L HF8 resulted in significantly higher MC-LR degradation ( $p < 0.05$ ) compared to that using 50 and 1000 mg/L HF8. After 60 min, only 1000 mg/L resulted in a significantly lower degradation compared to the other concentrations ( $p > 0.05$ ). With the increase of catalyst concentration, the degradation rate varied from 0.015 to 0.025  $\mu\text{g}/(\text{L min})$  calculated over the whole experimental period, with the maximum degradation rate obtained by using between 100 to 500 mg/L; with the use of both concentrations of catalyst resulting in a statistically similar effect as using 200 mg/L. After 60 min, the same activity was seen for all systems.



**Figure 2.** Effect of HF8 dose on the degradation of MC-LR. Data represent the average ratio of the MC-LR concentration per time point to initial concentration  $\pm$  standard deviation ( $n = 3$ ).

### 3.3. Effect of pH and nutrient anions

Because of the complexity of wastewater discharged from various industrial plants, the pH value could vary substantially, and therefore it was essential to study the effect of pH on the photocatalytic activity of HF8 for MC-LR degradation, in order to illuminate the applicability of HF8 for practical use. The removal of MC-LR was statistically constant irrespective of the pH value in the range of 3-11 ( $p > 0.05$ ), and therefore the data was not included. The wide working pH range of HF8 suggests that it could be a potential photocatalyst for the treatment of wastewater with varied pH values.



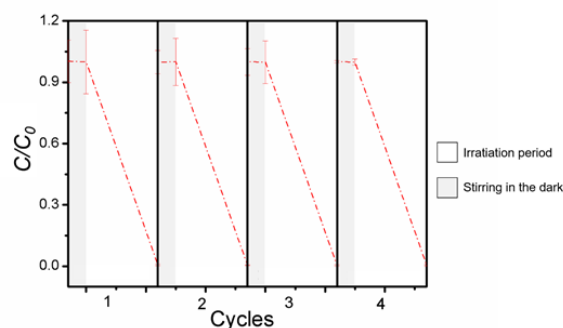
**Figure 3.** Degradation of MC-LR in the presence of NO<sub>3</sub>-and H<sub>2</sub>PO<sub>4</sub><sup>-</sup>. Data represent the average ratio of the MC-LR concentration per time point to initial concentration  $\pm$  standard deviation ( $n = 3$ )

MC-LR are commonly detected in the eutrophic waters; thus the influence of nitrogen (N) and phosphorus (P) present in high concentration in eutrophic waters were investigated by adding NO<sub>3</sub><sup>-</sup> and H<sub>2</sub>PO<sub>4</sub><sup>-</sup> at environmentally relevant concentrations as reported by [23]. As depicted in Figure 3, the presence of NO<sub>3</sub><sup>-</sup> and H<sub>2</sub>PO<sub>4</sub><sup>-</sup> had no effect on the degradation rate of MC-LR compared to in pure water ( $p > 0.05$ ).

### 3.4. Effect of recycling experiments of HF8 photocatalyst

Figure 4 shows the reusability of HF8 for remediation

of MC-LR within four cycles. Before light irradiation, the reaction mixture was stirred in the dark for 60 min to ensure adsorption equilibrium. Less than 2% of the MC-LR was removed during this process, demonstrating that the activity observed thereafter is not due to the adsorption of MC-LR on the catalyst, but to the photocatalytic action. In the reusability tests, the catalyst was filtered and reused directly without any treatment. No significant decrease in the rate of conversion between the four runs was observed ( $p > 0.05$ ), and the activity profile is visually identical for the four cycles indicating that the material is highly stable in the reaction and can be a potential catalyst for MC-LR degradation in practical application due to its continues reusability.



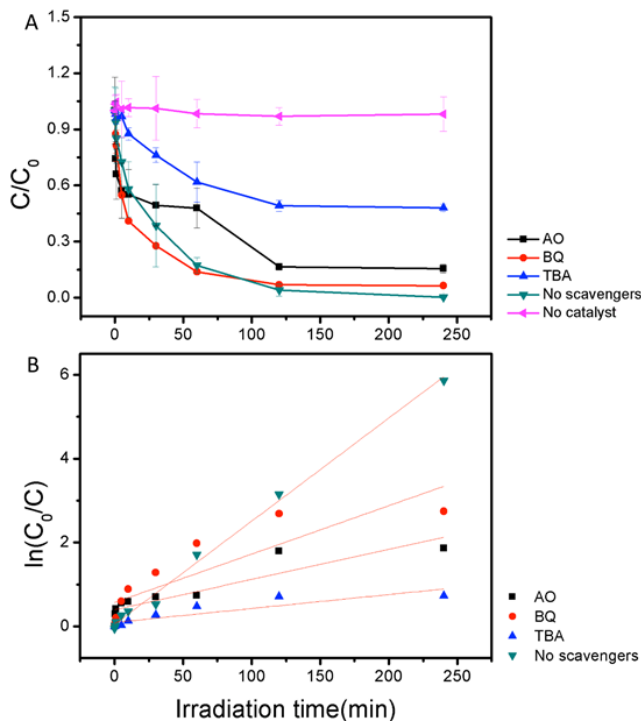
**Figure 4.** Reusability of HF8 for MC-LR photodegradation within four cycles

### 3.5. Roles of reactive oxygen scavengers

The influence of reactive species on MC-LR photodegradation by HF8 was investigated by adding three kinds of scavengers, namely AO, TBA, and BQ, which are used to quench the H<sup>+</sup>, the <sup>•</sup>OH, and the O<sub>2</sub><sup>•-</sup> species, respectively. Figure 5A shows that the three reactive species have very different effects on the reaction. By comparison, it was found that the influence of the scavengers is in order of BQ < AO < TBA, suggesting that the <sup>•</sup>OH has the most significant role, and the O<sub>2</sub><sup>•-</sup> species contributes the least to the reaction, in the sequence of <sup>•</sup>OH > H<sup>+</sup> > O<sub>2</sub><sup>•-</sup>. In other words, the <sup>•</sup>OH species is the primary factor responsible for the degradation of MC-LR.

The kinetics of MC-LR photodegradation in the absence and presence of scavengers were also calculated and are shown in Figure 5B. The  $k_{app}$  values obtained without the scavenger, and in the presence of TBA, AO, and BQ are 0.025, 0.003, 0.007, and 0.011 per min, respectively. The relationship between the ln

( $C_0/C$ ) and irradiation time supports the assumption that the reaction obeys the pseudo-first-order reaction, as discussed above.



**Figure 5.** Effect of scavengers on (A) the photodegradation activity of MC-LR over HF8; (B) Pseudo-first-order kinetics of MC-LR degradation over HF8

### 3.6. Potential breakdown-products of MC-LR catalysed by HF8

Structure elucidation of the MC-LR breakdown products as a result of advanced oxidation techniques using LC-MS/MS has been extensively covered in literature [30-32]. In general, the degradation seen is a function of small losses of  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ ,  $\text{CO}$ , and  $\text{CO}_2$ , as well as hydroxylation of the aromatic ring, methoxy group, conjugated double bonds, and Mdha amino acid. In the present study, some breakdown products were identified after the HF8 photolysis of MC-LR (Table 1). During photocatalysis, seven by-products, with  $m/z$  of 394.3, 401.2, 476.2, 332.1, 703.2, 330.3, and 307.2, were identified from the degradation of MC-LR. All the fragments had lower  $m/z$  values compared to the parent molecule ( $m/z$  of 995.5), which means that the breakdown products were cleaved into small or poly-charged ions.

**Table 1.** Fragmentation results for microcystin-LR (MC-LR) degradation breakdown products during photolysis processes

Time (min)	0	10	30	120	240	Potential structure
$m/z$						
394.3		+				
401.2		+	+			
476.2		+		+		
332.1		+		+		
703.2			+		+	
330.3			+	+	+	
307.2			+		+	

It is believed that the addition of a hydroxyl radical causes isomerisation at C4-C5 and C6-C7 of the diene bond in the Adda chain [3,5]. At first, the conjugated dienes in the Adda side chain are the initial targets of the electrophilic reactions. The hydrolysis and hydroxide radical attack at the Adda chain result in the separation of Adda from the peptides [31], which might produce the derivatives with the  $m/z$  394.3, 332.1, and 307.2, as also seen with HF8 in the present study. Other identified intermediates have an intact cyclic structure, i.e.  $m/z$  476.2, 401.2, and 703.2 were derived from the oxidation of double bond in the Mdha. It is proposed that MC-LR undergo hydrolysis at the MeAsp-Leu or Arg-MeAsp peptide bonds [33], these intermediates can be further hydrolysed by removal of amino acids, and then the cleavage of C4-C5 and further oxidation ( $\text{OH}$  attacks) may produce dihydroxylated intermediates of  $m/z$  703.2. Multi-step oxidation of Mdha and peptide bond yield to the double charged ions of  $m/z$  at 401.2. The product with  $m/z$

z 330.3 might be the fragment of Ala-Leu-MeAsp.

From the results of the present study, it is clear that the concentration of photocatalyst that needs to be applied should be optimised for each individual case where microcystin contaminated water is treated. In other respects, the results obtained after thorough testing clearly demonstrated HF8's applicability for MC-LR treatment in eutrophic water. Large-scale studies need to be performed; however, the data presented here shows the potential of this novel high-energy {001} faceted TiO<sub>2</sub> HF8 to be used in water treatment plants and for the restoration of lakes after bloom episodes.

## COMPETING INTERESTS

The authors declare that they have no competing interests.

## AUTHOR CONTRIBUTION

**Wu:** conception and design, or acquisition of data, or analysis and interpretation of data.

**Pflugmacher:** conception and design, interpretation of data.

**Yang:** conception and design.

**Esterhuizen-Londt:** conception and design, or acquisition of data, or analysis and interpretation of data.

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