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Pestana, C. J., Hobson, P., Robertson, P. K. J., Lawton, L. A., & Newcombe, G. (2020). Removal of microcystins from a waste stabilisation lagoon: Evaluation of a packed-bed continuous flow TiO₂ reactor. *Chemosphere*, 245, [125575]. <https://doi.org/10.1016/j.chemosphere.2019.125575>

Published in:
Chemosphere

Document Version:
Peer reviewed version

Queen's University Belfast - Research Portal:
[Link to publication record in Queen's University Belfast Research Portal](#)

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Removal of microcystins from a waste stabilisation lagoon: Evaluation of a packed-bed continuous flow TiO₂ reactor

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Declaration of Interest: None.

Highlights:

- Removal of microcystins from waste stabilisation lagoon
- Continuous flow, packed bed TiO₂ reactor design
- Significant removal of microcystins and improvement of water quality

- Natural organic matter decreases but does not inhibit microcystin removal
- Viable treatment option if optimised for toxin and cell removal

Graphical abstract:

Abstract

Photocatalysis has been shown to successfully remove microcystins (MC) in laboratory experiments. Most research to date has been performed under ideal conditions in pure or ultrapure water. In this investigation the efficiency of photocatalysis using titanium dioxide was examined in a complex matrix (waste stabilisation lagoon water). A flow-through photocatalytic reactor was used to photocatalyse four commonly occurring microcystin analogues (MC-YR, MC-RR, MC-LR, and MC-LA). Up to 51% removal for single MC analogues in waste lagoon water was observed. Similar removal rates were observed when a mixture of all four MC analogues was treated. Although treatment of MC-containing cyanobacterial cells of *Microcystis aeruginosa* resulted in no decline in cell numbers or viability with the current reactor design and treatment regime, the photocatalytic treatment did improve the overall quality of waste lagoon water. This study demonstrates that

despite the presence of natural organic matter the microcystins could be successfully degraded in a complex environmental matrix.

Keywords: waste water treatment; cyanobacteria; photocatalysis; titanium dioxide; microcystin

1. Introduction

Cyanobacteria commonly occur in waste stabilisation lagoons, usually applied to remove phosphates and nitrates, within waste water treatment plants (Barrington et al., 2013; Martins et al., 2011). Certain cyanobacterial strains are capable of producing toxic secondary metabolites; especially the microcystins (MC) are of rising worldwide concern and responsible for the intoxication of humans and animals (Ghadouani and Coggins, 2011; Paerl and Huisman, 2008). MC are hepatotoxic cyclic peptides with a wide variety of congeners (246 to date) (Spoof and Catherine, 2017); one of the most common and toxic congeners is MC-LR (LD_{50} in mice $50 \mu\text{g kg}^{-1}$) (Sivonen and Jones, 1999). The World Health Organisation has published a recommended maximum allowable level for MC-LR of $1 \mu\text{g L}^{-1}$ in drinking water (WHO, 2017). While the waste lagoon effluent is not destined for human consumption, it can be used for irrigation of crops and recreational areas or discharged into receiving water bodies (Barrington et al., 2013). While the health and safety risk is comparatively low when compared to drinking water MCs can nonetheless pose significant ecological issues. Additionally cyanobacteria and/or their secondary metabolites are known to hinder waste water treatment processes (Martins et al., 2011; Praptiwi et al., 2017).

Chemical oxidation with hydroxyl radicals (OH $\cdot$) generated by UV titanium dioxide (TiO $_2$) photocatalysis has previously been shown to successfully remove MC-LR and other congeners (Lawton and Robertson, 1999; Liu et al., 2002; Pestana, 2012; Pestana et al., 2015). However, there remain barriers to the application of this technology: the form of the catalytic material and subsequent separation of the catalyst from water, as well as the development of a continuous flow reactor to allow incorporation of the process in-line with treatment processes. Nano-particulate TiO $_2$ (e.g. Degussa P25) has a large reactive surface area (Lawton and Robertson, 1999; Robertson et al., 1997), however, separation from water is challenging and prevents ease of use. Pelletised TiO $_2$ facilitates separation from the sample matrix, however, effectiveness is reduced compared to nano-particulate TiO $_2$ (Liu et al., 2009). Coated surfaces have been demonstrated to be as effective as nano-particulates however, these require a specialised, energy demanding production process (Pelaez et al., 2010). Furthermore, previous studies (Lawton and Robertson, 1999; Liu et al., 2009, 2002; Pelaez et al., 2010; Robertson et al., 1997) evaluated removal of MC in pure water, whereas, in environmental applications other organic material would be present, competing with MC. Therefore, real-life applications will potentially experience decreasing effectiveness or alternatively requiring longer exposure times. Pestana et al. (2014) have recently successfully demonstrated the UV photocatalytic removal of the commonly problematic taste and odour compounds geosmin and 2-methylisoborneol with a packed-bed, continuous flow reactor using pelletised TiO $_2$ in water from a fish-farm raceway. This work demonstrated that a flow-through reactor design with pelletised TiO $_2$ is capable of removing trace water contaminants from a complex matrix.

In the present study, a bench scale packed-bed, continuous flow reactor was designed and used to demonstrate the UV photocatalysis of four commonly occurring MC congeners in waste lagoon water using pelletised TiO₂. Waste stabilisation lagoon water presents an extremely complex sample matrix with high dissolved organic material which present a challenge to the successful removal of toxic contaminants like MC, as natural organic matter (NOM) can exhibit radical scavenging properties and light attenuation. This represents an important step towards the implementation of the full-scale application of continuous-flow TiO₂/UV in water treatment applications.

2. Materials and methods

2.1 Chemicals

Hombikat K01/C titanium dioxide pellets (Supporting Information, S1) were obtained from Sachtleben Chemie (Germany) and rinsed thoroughly with reverse osmosis water (RO) before use for fines removal. Microcystin analogues were obtained from Enzo Life Science AG (Switzerland). All solvents were obtained from Merck (Germany) and were of analytical grade.

2.2 Photocatalysis of toxins

A packed-bed continuous flow reactor was constructed and connected to a 3 L reservoir. In brief, the reactor consisted of a three channel (connected in a serpentine fashion) sheet of polycarbonate with a guaranteed 95% UV permeability (Evonik, Germany) that was packed with pelletised TiO₂ (Sachtleben Chemie, Germany). Silicone tubing and a peristaltic pump recircled the test solution through the reactor (Supporting Information, S2). A test solution (autoclaved lagoon water or

RO filtered water) with $30 \mu\text{g L}^{-1}$ of the relevant microcystin analogue was prepared. In the case of the MC analogue mixture, $10 \mu\text{g L}^{-1}$ of each of the four analogues under investigation (MC-YR, -RR, -LR, -LA) were added. Initially, a T0 sample was taken, followed by the entire experimental volume of the reservoir passing through the reactor three times (contact time 1.9 min; see S2 for calculation of contact time) without irradiation to determine the dark absorption, i.e. the amount the MC concentration decreases in the absence of UV which is attributed to adsorption onto the TiO_2 . The time was deemed sufficient based on the results of the controls that were performed in the dark and the absence of UV irradiation (Supporting Information, S3). Following this, the test solution was recycled through the illuminated reactor for a total illuminated contact time of 14.3 min with samples taken at known intervals.

2.3 Photocatalysis of *Microcystis aeruginosa*

A 17 day old culture of *Microcystis aeruginosa* 338 (Australian Water Quality Centre) was aseptically separated from growth medium by centrifugation (15 min, $1640 \times g$ at room temperature). The cell pellets were re-suspended in waste lagoon water (100 mL). A sample was taken, fixed with Lugol's solution, and cell enumeration was performed using a Sedgewick-Rafter cell and light microscopy (Nikon 50i, Japan). The culture was analysed by flow cytometry using fluorescein diacetate (FDA) and SYTOX Green dyes to measure cell viability and membrane integrity using previously published protocols (Hobson et al., 2012). A cell suspension was prepared (3×10^5 alive cells mL^{-1}) in waste stabilisation lagoon water. The photocatalysis experiment was then performed as before (section 2.2) without the

addition of MC. Controls were performed in the absence of UV irradiation and in the absence of catalyst.

2.4 Analysis

Samples for MC analysis were concentrated by solid phase extraction (SPE) through C18 cartridges (Waters, United Kingdom) as previously described (Nicholson et al., 1994). After SPE the eluted samples were reduced to dryness by centrifugal evaporation in a MiVac DuoConcentrator attached to a MiVac DuoPump (both GeneVac, United Kingdom) and re-suspended in 50% aqueous methanol (1 mL), filtered (0.22 µm), and analysed by HPLC. The samples from the photocatalysis of the MC-containing *M. aeruginosa* were filtered (GF/C; Whatman, UK) to separate cells from the water. The filter disks containing the cells were frozen (-20 °C) then extracted in 10 mL of 80 % methanol for 60 min with occasional agitation (Lawton et al., 1994). The extract was reduced to dryness by centrifugal evaporation, re-suspended in 50 % methanol (1 mL), filtered (0.22 µm), and analysed. The MC in the cell filtrate was concentrated as before by SPE to determine extra-cellular MC concentration.

All processed samples were analysed on an Agilent Technologies 1100 series high performance liquid chromatography (HPLC) system consisting of a quaternary pump (G1311A), degasser (G1379A), auto sampler (G1313A), column compartment (G1316A) and photodiode array detector (G1315B) using the previously published method of Ho *et al.* (2006). The extraction recoveries for the above method are stated as > 95% (Ho et al., 2006a). Samples of treated and untreated waste lagoon water, along with the light and dark controls, were analysed by high performance size exclusion chromatography (HPSEC) for analysis of the effect the UV/TiO₂

treatment on the protein and humic portions of the NOM. For this, samples were analysed on a Waters Alliance 2690 separations module and 996 photodiode array detector (PDA) at 260 nm (Waters Corporation, USA) according to a method described in Fabris et al. (2008). A 0.1 M Phosphate buffer with 1.0 M NaCl was passed through a packed silica column (Shodex KW802.5; Showa Denko, Japan) at a flow rate of 1.0 mL min⁻¹. The effect of the treatments on water quality parameters was also monitored (Supporting Information S4).

3. Results and Discussion

3.1 Evaluation of reactor performance

Previously published studies of UV/TiO₂ removal have almost exclusively employed pure water, thus a comparison between the removal in pure water and waste lagoon water was performed. The matrices tested were RO water and waste lagoon water (see Supporting Information S4 for water quality parameters of untreated lagoon water). The removal of MC-LR dropped from 84% in RO water to 46% in waste lagoon water under the same experimental conditions (figure 1), with the most probable explanation being the presence of competing natural organic matter (NOM). Although another contributing factor could be the presence of inorganic ions that adhere to the TiO₂ and inactivate binding places by blocking them for organic molecules (Umar and Aziz, 2013), indicated by a decrease in conductivity from 1173 to 976 $\mu\text{S cm}^{-1}$ (Supporting Information, S4). Furthermore, NOM can act as a scavenger of the surface-generated oxidising species (e.g. OH and superoxide radicals) produced by interaction of the catalyst and the UV irradiation in the aqueous matrix (Feitz et al., 1999). Pelaez et al. (2011) also found that NOM had an inhibitory effect on the photocatalysis of MC-LR when they investigated the

photocatalytic breakdown of MC-LR both in the presence of naturally occurring humic and fulvic acids.

Figure 1: Removal of MC-LR (initial concentration $30 \mu\text{g L}^{-1}$) in TiO_2/UV packed-bed flow-through reactor comparing efficiency in pure water (RO filtered water) - ■ and waste lagoon water - □. (Error bars=1 SD, $n=2$)

In the work of Pelaez et al. (2011) the adsorption of NOM to TiO_2 at different pH levels was investigated and it was found that the adsorption of NOM to the surface of the catalyst increased with decreasing pH, with highest adsorption rates observed under acidic conditions (pH 3.0). Other research has suggested that under acidic conditions another competing process could operate. Paul et al. (2007) suggested that the adsorption of fluoroquinolone (a synthetic antibiotic) to TiO_2 could lead to the formation of a surface coordination complex that could facilitate the transfer of electrons from the conduction band of TiO_2 to an appropriate electron acceptor, thus

209 inhibiting the formation of the hydroxyl radicals that lead to the mineralisation of the
210 target analyte. Pelaez et al. (2011) proposed that NOM might perform the same
211 function, this, however, is unlikely as the neutral to mildly alkaline range (pH 8.0)
212 ensures that the NOM predominantly acts as a radical species scavenger.

213 Thirumavalavan et al. (2012) have proposed that NOM and increased turbidity can
214 hinder the photolysis of MC-LR at the UV irradiation wavelengths employed in the
215 current study by reducing transmittance and light absorption. This would further
216 account for the decreased removal of MC-LR in the waste lagoon water compared
217 with the RO filtered water. He et al. (2012) also reported that NOM had a negative
218 impact on MC removal their study, albeit much lower concentrations of both toxin
219 and NOM were used/present in that study which was conducted in natural water
220 samples from a lake and a river. Autin et al. (2013) demonstrated that background
221 organic matter not only acts as a scavenger but may also saturate the catalyst's
222 surface in their study investigating the photocatalytic degradation of the pesticide
223 metaldehyde by UV/H₂O₂ and UV/TiO₂. Khan et al. (2010) showed that the humic
224 portion of NOM can also attenuate the incidental irradiation due to their light
225 absorbing properties when investigating the photocatalysis of brevetoxins in the
226 presence of humic acid.

227 High performance size exclusion chromatography (HPSEC) analysis of the protein
228 and humic acid portion of the organic matter in waste water can demonstrate the
229 removal of organic compounds other than the target analyte (Figure 2). Results
230 indicate that the concentration of the humics and proteins decrease slightly in the
231 control samples (figure 4 B and D) possibly due to photolysis in the UV only control
232 and surface adsorption onto the TiO₂ in the dark control. More significant changes,
233 however, were observed in the protein and humics profiles following photocatalytic

treatment (figure 4 A and C) with the general trend in reduction in apparent molecular weight for both analyte groups suggesting significant degradation has taken place, reducing larger molecules to smaller fragments. Furthermore, the overall intensity of the signal for both proteins and humics has been reduced by around a third. This confirms that photocatalysis of the NOM occurs concurrently with the photocatalysis of MC accounting for the reduced MC removal efficiency in the waste lagoon water demonstrating, as might be expected, that UV/TiO₂ oxidation is non-selective. Another indicator of this is the fact that most of the water quality parameters improve, such as UV absorbance and transmittance at 254 nm (also indicative of NOM removal), colour and turbidity (which is in part due to NOM removal and in part due to the reactor acting as a filter), and dissolved organic carbon (again indicative of NOM removal; Supporting Information, S4).

Figure 2: HPSEC determination of protein content (A and B) and humic acid content (C and D) in untreated waste lagoon samples and in UV/TiO₂ treated waste lagoon samples, and control samples (UV and dark controls).

3.2 Evaluation of MC congener destruction in waste lagoon water

Single microcystin analogues in waste lagoon water were passed through the reactor (Figure 3). The amount of dark adsorption (the initial binding of an organic pollutant to the titanium dioxide in the dark) can be an important determining factor in the removal rate of that pollutant (Feitz et al., 1999; Linda A Lawton et al., 2003). It has been observed in previous studies (Linda A Lawton et al., 2003; Pestana, 2012; Pestana et al., 2015) that the amino acid composition at the variable amino acid site impacts the dark adsorption of a given microcystin analogue.

Figure 3: TiO₂/UV packed-bed flow-through reactor removal of four individual microcystin analogues (30 µg L⁻¹, respectively) in waste stabilisation lagoon water. (Error bars=1 SD, *n*=2)

In the present study, the four MC variants display slightly different dark adsorption ranging from 7% (MC-RR) to 17% (MC-YR). Direct comparison with previous studies is difficult as systems, including catalyst, light source, and physicochemical parameters vary significantly. Furthermore, the presence of NOM in the waste stabilisation lagoon water would further impact the dark adsorption of the MC analogues, due to competition for the binding sites on the catalyst, as was also observed by Autin et al. (2013). Despite the presence of NOM, and inorganic ions that can inhibit UV/TiO₂ photocatalysis (Khan et al., 2010), in the water, breakdown of all four microcystin analogues can be observed. MC-YR underwent the greatest removal (51%) after 14.3 min exposure time, followed by MC-RR 48%, and MC-LR with 46% removal which all demonstrate similar efficiency. However, removal of MC-LA was much lower, with around half the efficiency (28%) showing an initial decline of around 20% in the first 5 min but removal slowing dramatically so that less than 10% is degraded in the subsequent time (9.3 min). One possible explanation for the lower oxidation of MC-LA may be due to the fact that the point of zero charge (pH_{zpc}) for TiO₂ was determined to be pH 6.25 (Hoffmann et al., 1995), which means that below this value the surface of the TiO₂ is positively charged and above this value the surface becomes negatively charged. According to Lawton and co-workers (Linda A Lawton et al., 2003), if the pH of the test solution is greater than the pH_{zpc} the oxidation of cationic species would be favoured, whereas if the pH of the test solution is lower than the pH_{zpc} the oxidation of anionic species would be favoured. This suggests that the oxidation of MC-LA is not favoured in the current study (initial pH of test solution 8.0) considering the net charge of MC-LA at pH 7.4 is -2

(Herfindal et al., 2009). While the net ionic charge of MC-YR, MC-LR, and MC-RR may have been anionic (Rivasseau et al., 1998), they are less than MC-LA (predicted charge of 0 or -1), which may explain the increased destruction of these analogues compared to MC-LA. Furthermore, it was determined by Rivasseau et al. (1998) that MC-YR is the least hydrophobic of the three MC they investigated, followed by MC-LR, and finally MC-RR at pH 7, leading to MC-LA being less likely to be adsorbed onto the catalyst surface. While surface adsorption is not essential for degradation, it has been suggested that when molecules are adsorbed the surface they are held in close proximity to the site of hydroxyl radical production (Lawton et al., 2003), hence their degradation is more efficient. Rivasseau and co-workers (1998) also found MC-YR was adsorbed (13% at pH 6.7) to natural suspended matter in river water samples slightly more so than MC-LR (11%), and MC-RR (9%). These observations are similar to those in the current study with initial adsorption: MC-YR 17 %; MC-LR 11%; MC-RR 7 %. The results in the present study agree with previous studies (Lawton et al., 2003; Pestana et al., 2015; Shephard et al., 1998), that the efficiency of removal of different microcystin analogues in a photocatalytic system will depend on the variable amino acid composition of the MC analogue (and pH of the system) due to charge, hydrophobicity influences, and the differing susceptibility of various amino acid groups to oxidation, which was demonstrated in oxidation by chlorination where a reactivity order of MC-YR>MC-RR>MC-LR>MC-LA has been found (Ho et al., 2006b).

In addition to determining the photocatalytic efficiency of the reactor with single MC analogues, a mixture of all four analogues was investigated to determine whether direct competition affected the photocatalysis of the different MC (Figure 4).

Figure. 4: TiO₂/UV packed-bed flow-through reactor removal of a mixture of four microcystin analogues (10 µg L⁻¹ of each analogue) in waste stabilisation lagoon water. (Error bars=1 SD, *n*=2)

The amount of dark adsorption remains constant for three of the variants (MC-LR increases slightly from 8 to 11%) suggesting little competition between the analogues as might be expected considering the relative concentrations of the analogues compared to the other dissolved organics (DOC 23.8 mg L⁻¹; Table S3). Despite much lower background interference in their study Rimoldi et al. (2017) also reported no decreased removal of their target analytes (tetracycline, caffeine, paracetamol, atenolol) by TiO₂ photocatalysis when they were present in a mixture. The removal of MC-RR, MC-LA and MC-LR remained very similar (3% less removal for MC-LA and-LR) while the removal of MC-YR was also similar there was an increased from 51 to 59%. This confirmed that MC-YR is more readily removed than the other three analogues, regardless of whether it was treated as a single or mixed array of MC. This will be of relevance in applying this technology to naturally MC contaminated water because it has often been observed that multiple MC are

335 present during bloom events. Furthermore, it demonstrates the importance of not
336 directly extrapolating predicted efficiencies from trials with different analogues.

337 The mechanism of the photocatalytic destruction of microcystins has been previously
338 reported in a number of detailed studies by Liu *et al.* (2003), Song *et al.* (2007) and
339 Antoniou *et al.* (Antoniou *et al.*, 2008a, 2008b). Using LC-MS to identify by-products
340 of the photocatalytic process, Liu *et al.* suggested the main processes involved in the
341 photocatalytic decomposition process were a UV photo-isomerisation followed by
342 hydroxyl radical attack and direct oxidation of the microcystin molecule. Song *et al.*
343 proposed that UVC light would be required for the photo-isomerisation process and
344 this could not be initiated by UVA light. Antoniou *et al.* [45] subsequently proposed
345 that the isomerisation may have been induced by hydroxyl radical attack on the
346 diene bonds of the ADDA group on the microcystin. Again using LC-MS to identify
347 intermediates, Antoniou and co-workers [46] reported a total of eleven new
348 intermediates that were not detected in the study by Liu *et al.* It should be noted that
349 this study was conducted at pH 5.7 using immobilised film reactors, while Liu used a
350 slurry reactor. The complex matrix (waste water) used in the current study prevented
351 the elucidation of degradation (by-)products. A common concern in the degradation
352 potentially harmful pollutants is the danger represented by degradation products
353 displaying a similar, or, in fact, higher toxicity than the parent molecule. This is not
354 usually the case for microcystins. As elucidated by the studies of Antoniou *et al.*
355 (2008a, 2008b), the first location of hydroxyl radical attack is the ADDA moiety of the
356 microcystin molecule. The attack in several steps changes the arrangement of this
357 moiety (Antoniou *et al.*, 2008a). Several studies have shown that the ADDA moiety is
358 primarily responsible for the toxicity of microcystins (An and Carmichael, 1994;
359 Dawson, 1998; Luukkainen *et al.*, 1994; Trogen *et al.*, 1996), therefore it can be

concluded that the degradation intermediated of the photocatalytic removal of microcystins does not lead to the creation of more toxic compounds, but rather a detoxification of the solution.

3.3 Photocatalysis of *Microcystis aeruginosa* cells

Evidence from the literature suggests that titanium dioxide is capable of inactivating cyanobacteria (Hong et al., 2005; Kim and Lee, 2005). According to Malato et al. (2009) the susceptibility of microorganisms to photo-inactivation is (from least to most susceptible): protozoa, bacterial spores, mycobacteria, viruses, fungi, bacteria. Furthermore, there is a ranking of susceptibility within the group of bacteria with Gram-positive bacteria being less susceptible than Gram-negative bacteria due to differences in the structural complexity of the cell wall (Lydakis-Simantiris et al., 2010). According to the aforementioned ranking the common MC-producing cyanobacteria *M. aeruginosa* which has a Gram negative cell wall should show susceptibility to photocatalytic inactivation. Treatment in the packed-bed flow-through reactor found that the photocatalytic process had no effect on cell numbers (Supporting Information, S5). The number of cells remains stable in the treatment as well as the two controls (UV control and dark control). It is likely that reactor design, while effective for dissolved MC, is not appropriate for the treatment of cyanobacterial cells. When successful removal of microorganisms is reported in the literature they typically report the use of a static system, nano-particulate or thin film catalysts, and/or long contact times (Baram et al., 2011; Benabbou et al., 2011; Hong et al., 2005; Kim and Lee, 2005; Prasad et al., 2009; van Grieken et al., 2009a, 2009b). The flow-through system used in this study provided only limited treatment exposure (14.3 mins), which may not be sufficient considering other studies (Hong et

al., 2005; Kim and Lee, 2005) where test solutions were exposed between 60 mins and four days. The study did, however, show that extracellular MC (MC-LR, -YR, -RR) released from the *M. aeruginosa* were photocatalysed (figure 5).

Figure 5: TiO₂/UV packed-bed flow-through reactor removal of intra- (A) and extra-cellular (B) MC during the photocatalytic treatment of *M. aeruginosa* in waste stabilisation lagoon water. (Error bars=1 SD, *n*=2)

High concentrations of MC-RR (68 $\mu\text{g L}^{-1}$) were found to be present in the culture and a reduction in MC-RR concentration of 28% was observed. Lower concentrations of MC-LR and MC-YR were also detected (8.6 and 3.4 $\mu\text{g L}^{-1}$,

respectively) which also degraded (48 and 24%, respectively). These findings demonstrate that while whole cyanobacterial cells were unaffected by photocatalysis, the levels of dissolved MC analogues were reduced. A further indicator that the cells were not disrupted cell is that intra-cellular MC levels do not change during the photocatalysis.

3.5 Conclusion

The prevalence of microcystins in waste water can have serious implications for public health and safety depending on waste water effluent utilisation. Irrigation of food crops or of recreational areas can lead to human and animal intoxication, release into streams/rivers carries similar risks. This investigation has demonstrated the practical application of TiO₂ photocatalysis for waste stabilisation lagoon effluent treatment. The current reactor configuration readily lends itself to a larger scale application: The packed-bed nature of the design removes the challenge of catalyst separation post treatment and the continuous flow ensures that effluent can constantly be treated without the need to revert to a batch application. One area the current reactor design could be improved on is the UV irradiation source, however, it was demonstrated in a previous study (Pestana, 2012) that UV light emitting diodes could easily replace the need for high powered and energy inefficient UV lamps. The presence of NOM in waste water effluent challenges the removal of MC, but as has been demonstrated does not negate the removal by photocatalysis. Using a TiO₂ packed-bed flow-through reactor full-scale application could provide a low maintenance, low cost treatment for the elimination of cyanotoxins (and other trace toxic pollutants) in low quality water in a format which could be deployed in diverse environments across the globe.

Supporting Information

Additional information about the rationale behind catalyst selection (section S1), a detailed description of the reactor design (section S2), light and dark controls for the removal of MC-LR from waste stabilisation lagoon water (section S3), a detailed analysis of water quality parameters in untreated, UV/TiO₂ treated and control samples (section S4), and cell viability data for the photocatalysis of *M. aeruginosa* (section S5).

Acknowledgements

This research was funded by the Australian Government Department of Education and Training through the Endeavour post-doctoral award (C.J. Pestana) and the Engineering and Physical Sciences Research Council (EPSRC) UK [EP/P029280/1].

The authors would like to thank Senior Technician Martin Harris and Laboratory Manager Edith Kozlik for the analysis of the toxin samples, DOC, and HPSEC analysis. Furthermore, the authors would like to thank Len Montgomery for proof-reading the manuscript.

The authors declare no competing financial interest and no influence was taken by the funding source on the study design, conduct of the research and/or preparation of the article.

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