Photocatalytic degradation of eleven microcystin variants and nodularin by TiO₂ coated glass microspheres

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Abstract

Microcystins and nodularin are toxic cyanobacterial secondary metabolites produced by cyanobacteria that pose a threat to human health in drinking water. Conventional water treatment methods often fail to remove these toxins. Advanced oxidation processes such as TiO_2 photocatalysis have been shown to effectively degrade these compounds. A particular issue that has limited the widespread application of TiO2 photocatalysis for water treatment has been the separation of the nanoparticulate power from the treated water. A novel catalyst format, TiO_2 coated hollow glass spheres (Photospheres™), is far more easily separated from treated water due to its buoyancy. This paper reports the photocatalytic degradation of eleven microcystin variants and nodularin in water using Photospheres™. It was found that the Photospheres™ successfully decomposed all compounds in 5 minutes or less. This was found to be comparable to the rate of degradation observed using a Degussa P25 material, which has been previously reported to be the most efficient TiO_2 for photocatalytic degradation of microcystins in water. Furthermore, it was observed that the degree of initial catalyst adsorption of the cyanotoxins depended on the amino acid in the variable positions of the microcystin molecule. The fastest degradation (2 minutes) was observed for the hydrophobic variants (microcystin-LY, -LW, -LF). Suitability of UV-LEDs as an alternative low energy light source was also evaluated.

1. Introduction

Cyanobacteria and their secondary metabolites, in particular their toxins, pose a serious health hazard to both humans and animals. Failure to control the propagation of cyanobacteria can result in the production of potent toxic secondary metabolites in aquatic systems. The management of cyanotoxins is important when considering water safety, especially for potable use. Consequently the removal of these toxins during water treatment is a key concern. The photocatalytic destruction of cyanotoxins using TiO_2, particularly microcystin-LR, has been studied in detail and reported to be a very effective process for removal of these toxins from water [1-9]. The implementation of this technology by the water treatment sector, however, has been limited due to the difficulties encountered in overcoming post-treatment catalyst removal [10]. Three main ways of deploying TiO_2 as a semi-conductor photocatalyst in water treatment have been examined. The materials have been deployed as (nanoparticulate) powders, as pellets, or as films attached to appropriate substrates [11-13]. Powders generally perform well in the photocatalytic degradation of organic compounds due to their large surface area and effective distribution in suspension. Nevertheless, a significant challenge faced when using powders is the separation of the powder suspension from the treated water [11]. Pelletised photocatalysts may address the issue of catalyst separation, however, such materials tend to perform less efficiently in comparison to the powders [10]. Another disadvantage of pelleted photocatalysts is the fact that vigorous mixing can cause the pellets to fragment, releasing free catalyst powder which results in the same issue of removal that is encountered when using powders [10]. Photocatalysts can also be deployed as a fixed matrix, usually as a film or in the form of nano tubes/rods. Preparation of these materials, however often requires convoluted and cost-intensive manufacturing

processes, and they also have a reduced reactive surface area compared to powder and pelletised materials [11,14]. A novel approach for deploying photocatalysts is annealing the materials to hollow, buoyant glass spheres. The size of these products ranges from the micro to millimetre. One of these novel products, known as Photospheres™ (Table 1), are hollow buoyant TiO_2 coated glass beads, which were developed by Nanoparticulate Surface Adhesion Ltd. (NSA Ltd.). Photospheres™ are hollow glass beads (40µM diameter) coated with 100 % anatase TiO_2 [15].

Insert Table 1 here

Due to the buoyancy of these materials they can be easily separated from treated water, however, they still provide a high surface area. A number of researchers have previously reported the use of TiO_2 coated spheres or spheres formed from titania for decomposition of contaminants in water [16-21]. Li *et al.* [16, 17] successfully degraded methylene blue and orange II with titanium dioxide covered hollow silica spheres. Zhao *et al.* [18] successfully degraded rhodamine B under visible light with hollow spheres (Si/Ti hybrid) of Ag doped titania. Ren *et al.* [19] produced hollow mesoporous TiO_2 coated microspheres, however, they did not assess their photocatalytic efficiency. There have also been two studies which have reported the use of titania covered silica spheres of larger diameter (mm) for the control of algae/cyanobacteria [20, 21]. These studies successfully targeted the growth of the organisms but did not explore the removal of any of their harmful metabolites.

Photospheres™ combine the high surface area of particulate catalysts with buoyancy. Jiang evaluated Photospheres™ for the photocatalytic destruction of dimethyl phthalate and reported an optimum photocatalyst loading and irradiation

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time of 8 g/L and 20 minutes respectively [22]. To date, no data has been published examining the photocatalytic removal of microcystins using TiO_2 coated microspheres. This study is the first report of the application of Photospheres™ in the photocatalytic degradation of eleven microcystin (MC) variants and nodularin in water. While MC-LR is widely held to be the most commonly occurring microcystin, it rarely occurs alone and to date many variants have been described [23]. It is therefore important that a wide range of microcystin variants are evaluated to ensure that degradation kinetics are comparable across a range of microcystin structures.

2. Experimental

2.1 Materials

Photospheres™ were purchased from NSA Ltd., Loanhead, UK. Microcystin variants and nodularin were obtained as per Edwards *et al.* [24] (Enzo Life Sciences, Farmingdale, USA). In addition to nodularin the microcystin variants studied included microcystins -LR, -RR, -LA, -YR, -LY, -LW, -LF, HtyR, methylated microcystin-LR and demethylated microcystins -LR and -RR. HPLC solvents were acetonitrile (Rathburn, Walkerburn, UK) and Milli-Q water (Millipore, Watford, UK), trifluoroacetic acid (TFA) was obtained from Fischer Scientific, Leicestershire, UK. All aqueous solutions were prepared with Milli-Q water.

2.2 Photocatalysis

The photocatalytic method was derived from that reported by Robertson *et al.* [25]. A 13 mm, 4 mL screw top vial (Kinesis, Beds, UK) with a plastic lid with a self-healing rubber septum and silicon facing was filled with a 10 µg mL^{-1} solution (3 mL) of a

microcystin variant or nodularin. One significant difference from previous protocols was the application of mixing by air sparging as opposed to mechanical stirring as previously described. Initial tests found that gentle stirring was not sufficient to mix the catalyst throughout the reaction vessel due to its tendency to float. More vigorous mixing, however, caused physical damage to the spheres as described by Mozia *et al.* [26]. The test solution was air sparged by inserting a hypodermic needle through the rubber septum of the vial and into the solution. Air flow was controlled via silicon tubing connected to a rotameter (Influx Measurements, Alresford, UK), which, in turn, was connected to an air pump (JUN-AIR, Nørresundby, Denmark; figure 1). The airflow was maintained at 0.2 cm^3 min^{-1}. The reaction vessel was placed in front of a Xenon lamp (480 W UVASpot 400 lamp, Dr Hönle UK, spectral output 330-450 nm, light irradiance: 1230 µmol s^{-1} m^{-2}) at a distance of 20 cm. One hundred twenty µL samples were removed at the beginning of the experiment (T_{01}) prior to the addition of the photocatalyst allowing the initial concentration of analyte to be determined. Subsequently the catalyst (1 % w/v TiO_2; equivalent to 5.88 g Photospheres™ per 100 ml, suspension pH 5.12) was added to reaction vessel, mixed, then kept in the dark for a further two minutes, after which another sample was taken (T_{02}, indicative of dark adsorption). The vial was subsequently exposed to the UV light source and samples were taken at 1, 2, 3, 4, 5, 6, 8, and 10 minutes. Prior to analysis catalyst was removed from the solution by small volume centrifugal filtration (5 minutes (2000 x g) at room temperature in Spin-X filters, 1.5 ml (Corning B.V. Life Sciences, Amsterdam, The Netherlands). Two controls were performed: one in the dark to confirm that decrease in concentration was due to photocatalytic activity alone, and one without the catalysts present to assess the possible effect of UV irradiation alone on the target analytes. All treatments were performed in duplicate. The photocatalytic

degradation of each microcystin and nodularin was determined individually with an initial concentration of 10 µg mL^{-1} in water. To compare the toxin destruction on Photospheres with that on the Degussa P25 material (Evonik Industries AG, Essen, Germany) the degradation of MC-LR was performed with 1% w/v of the photocatalyst with the pH of the P25 slurry at 5.33.

Insert figure 1 here.

2.3 Photosphere™ catalyst load and re-use

The effect of different catalyst loads on the photocatalytic degradation of microcystin-LR was assessed. The experiments were carried out as described (section 2.2) using a catalyst loading of between 0.2 % (w/v) TiO$_2$ and 1 % (w/v) TiO$_2$ in 0.2 % increments.

Photosphere™ re-use for the degradation of MC-LR was evaluated using the same initial set-up, however, sampling was only performed at 5 minutes. After sampling the reactor was irradiated for a further 5 minutes to deplete the remaining MC-LR then a new aliquot of MC-LR (10 µg mL^{-1}) was added to the catalyst suspension. This was repeated ten times.

2.4 Performance of Photospheres™ under UV-LED illumination

The recent increased availability of low energy UV-LEDs has prompted a number of investigations into their application in photocatalytic waste remediation [26-30]. A small scale reactor was designed to illuminate a 4 mL (13 mm diameter) glass screw top vial centred in a ring of 30 LEDs. The reactor (PVC tube 51 x 45 mm, 4 mm wall) was constructed by inserting LEDs in pre-drilled holes configured in three rows. The UV-LEDs (AT Technologies, Bath, UK) had a diameter of 5 mm, a 15° aperture, λ

360 nm, and a power output of 750 µW at 20 mA DC /3.8 V. Each chain of 10 LEDs was connected in series. The three LED chains were in turn connected in parallel. The distance between the wall of the screw-top vial and the LEDs was 1.5 mm. The degradation of MC-LR under UV-LED was evaluated for both Photospheres™ and Degussa P25 with all other aspects of the photocatalysis as described (section 2.2)

2.5 Analysis

Analysis was performed by HPLC using a Waters 2695 Separation Module. High resolution photodiode detection was performed with a Waters 2996 Photodiode Array Detector (PDA) (both Waters, Elstree, UK). Separation of analytes was performed with a Sunfire C18 column 2.1 mm (inner diameter) x 150 mm, with a 5 µm particle size (Waters, Elstree, UK). The mobile phases used were Milli-Q and acetonitrile, both contained 0.05 % trifluoroacetic acid (TFA). Chromatography was achieved over a linear gradient from 15% to 65% acetonitrile for 10 minutes followed by a 100% solvent wash and equilibration. The flow rate applied was 0.3 mL min^{-1}. The PDA resolution was set to 1.2 nm and data was acquired in the range of 200 to 400 nm. Column temperature was set to 40°C [25].

3. Results and Discussion

3.1 Photocatalysis

Eleven microcystin variants and nodularin were irradiated in the presence of the titanium dioxide coated Photospheres™. Results indicated that none of the microcystin variants or nodularin were detected after five minutes continuous UV irradiation time (Table 2).

Insert Table 2 here

Microcystin-LW, -LF, and -LY degraded fastest, with no detectable toxin remaining after two minutes irradiation. Nodularin and Microcystin-HtyR degraded more slowly with no detectable toxin remaining after four and five minutes respectively. There were differing levels of the extent of dark adsorption to the photocatalyst surface for the various microcystin variants with the rate of toxin degradation varying between two and five minutes. Lawton *et al.* [32], previously reported that different microcystin variants displayed different levels of dark adsorption on nanoparticulate Degussa P25 powders. Similar trends appeared to follow for the microspheres examined in this investigation. The results clearly showed that the amount of dark adsorption of microcystins to TiO_2 was dependent on the variable amino acid in the various microcystin structures. The more hydrophobic microcystins, which contained leucine at the variable position 4 and hydrophobic amino acids in position 2 (e.g. microcystin-LW and -LF), tended to show a greater level of adsorption compared to microcystin-RR which contained the more polar arginine at both variable positions. This was also observed in Lawton *et al.'s* previous study on P25 TiO_2 powders with its conclusion that the hydrophobicity of the target analyte also played a role in dark adsorption to the photocatalyst [33]. They also reported that the more hydrophobic microcystin variants (microcystin-LW and microcystin-LF) had a higher level of dark adsorption (at pH 4) than the less hydrophobic variant microcystin-RR. While the overall extent of dark adsorption in this study differed in direct comparison, the general relationship remained the same with microcystin-RR having the lowest dark adsorption and microcystin-LW the highest. The comparative difference in the amount of dark adsorption was most likely due to the properties of different catalysts used. Degussa P25 has a BET surface area of approximately 50 m^2 g^{-1} [33],

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whereas Photospheres™ only have a BET surface area of approximately 27 $m^2\ g^{-1}$ [15]. Another factor that could influence dark adsorption might be steric hindrance posed by one, both, and/or the combination of the variable amino acids. Nodularin, the smaller pentapeptide cyanotoxin was found to demonstrate the lowest dark adsorption. Liu *et al.* [34] previously reported successful photocatalytic decomposition of nodularin with TiO_2 (Degussa P25), however, dark adsorption differed greatly between that study and the present investigation (44 % compared to 14 %). Nonetheless, in the present study nodularin was undetectable within 4 minutes. These differences can be explained by the different components used in the two studies (e.g. glass vessel thickness, mode of agitation, distance to light, toxin concentration, and catalyst concentration).

Feitz *et al.* [35] and Lawton *et al.* [32] both reported a clear correlation between the amount of dark adsorption and microcystin decomposition with the most effective toxin removal being achieved where there was the greatest level of dark adsorption. This observation, however, conflicts with a number of the microcystin variants examined in this study. Microcystin-YR and methylated microcystin-LR displayed a very similar level of dark adsorption (45 and 46 % respectively). When compared to microcystin-LY (48 %), microcystin-YR and methylated microcystin-LR take twice as long to degrade to a level where it was no longer detected. Furthermore, microcystin-RR degrades almost twice as fast as Microcystin-HtyR, while having about half that variant's dark adsorption, although as stated above the overall difference in degradation times between the different variants is relatively marginal.

Further studies exploring the catalytic degradation of different microcystin congeners have recently been reported by He *et al.* [36] who examined the influence of variable amino acids on the rate of degradation and mechanism of the destruction on four

microcystin variants, -LR, -YR, -RR and -LA, by both direct UV photolysis and three advanced oxidation processes, including UV/H_2O_2, $UVS_2O_8^{2-}$ and UV/HSO_5^-. They reported that the variable amino acid not only influenced the overall rate of degradation but also the reaction mechanism.

The degradation of microcystin-LR in the presence of 40 micron Photospheres™ and Degussa P25 powder photocatalyst was compared (Figure 2). Encouragingly it can be clearly seen that the degradation of the cyanotoxin using the Photospheres™ is comparable with that achieved on the powder photocatalyst with the toxin being decomposed within four minutes for both materials.

Insert Fig 2 here.

The decomposition of the toxin on both materials was also achieved under UV/LED irradiation (Fig 3). Due to the lower photonic output of the LED arrays used in this investigation the decomposition rates of microcystin-LR using both P25 and 40 micron Photospheres™ were slower than that observed under the xenon source. In the case of P25 complete destruction of the toxin was achieved within 10 minutes under UV LED irradiation, compared to four minutes under the xenon lamp. Using the Photospheres™, however, over 30% of the microcystin remained after 10 minutes UVLED irradiation. The slower kinetics under UV LEDs is not surprising as the influence of light intensity on the photocatalytic process has long since been established [37]. The Photospheres™ appear to have been more significantly influenced by the reduction in light intensity under the LED irradiation compared to the P25 powders which may reflect the lower surface area of the Photospheres™. Despite the reduction in removal efficiency the potential cost saving benefits of UV LED illumination are worth considering with UV LED lamp life estimated at c.

100,000 hours compared to typical 1,000 hours for UV gas discharge sources. Furthermore, the energy demand of the Xenon lamp used in this study was 450 Watts compared to the UV LED array with a radiant power of 12.05 mW. These findings suggest significant efficiency gains can be made in designing treatment systems based on LED technology.

Insert Fig 3.

3.2 Photosphere™ catalyst load and re-use

A series of catalyst loadings (0.2, 0.4, 0.6, 0.8, and 1.0 % TiO_2) were tested. It was found that while photocatalytic decomposition improved for loadings between 0.2 to 0.4, and 0.4 to 0.6 % (w/v) TiO_2, only modest increases in photocatalytic efficiency were obtained for catalyst concentrations of 0.6 % (w/v) TiO_2 and above (Fig 4a). This suggests that catalyst loadings of less than 1 % could achieve the desired degree of toxin removal, in water treatment systems, reducing the overall cost of the process. The relationship between catalyst loading and photocatalytic efficiency for powder photocatalysts is well established [38, 39], with the optimal loading ranging reported between 0.1 and 0.5 g L^{-1}. Jiang et al., [22] reported optimum performance of Photospheres™ at a dose of 8 g/L (0.8 %), and while the compounds being treated were different, this is similar to the findings reported here. A linear relationship between catalyst loading and the amount of dark adsorption was observed (Fig 4b) for the range of catalyst loadings examined which would be anticipated.

Insert Figure 4 here

The repeated use of the Photospheres™ for the degradation of microcystin-LR has also been successfully demonstrated, with the photocatalytic efficiency for toxin decomposition being maintained for up to ten cycles. This suggests that the Photospheres™ could be recycled for continuous use in a water treatment process, while maintaining their photocatalytic efficiency. Mozia *et al.* [26], however, previously reported that over prolonged use in an aerated batch reactor the Photospheres™ started to degrade and lose their buoyancy. In this study the Photospheres™ appeared to maintain their integrity, buoyancy and photocatalytic activity between repeated tests, however, treatment conditions may have to be carefully designed to minimise damage.

4. Conclusion

It has been demonstrated that TiO_2 coated silica spheres (Photospheres™) can effectively decompose a range of microcystin variants and nodularin under UV radiation. The rate of reaction was comparable to that achieved over a P25 photocatalyst for microcystin-LR. All the microcystin variants and nodularin were degraded within less than five minutes concentrations above which these toxins are usually detected in the environment. Degradation of microcystin-LR was also achieved under UV LED irradiation for both P25 and Photospheres™, although the rate of decomposition was significantly lower due to the lower photonic output of the UV LEDs compared to the Xenon source. This suggests that UV photocatalysis with Photospheres™ could be a viable method for the treatment of water contaminated with microcystin and/or nodularin. Further research is required to determine the viability of the application in more complex matrices and at more environmentally relevant concentrations.

Acknowledgements

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List of Captions for Figures.

Fig. 1 Photocatalytic reactor for Toxin Destruction using Photospheres™

Fig. 2 Photocatalytic degradation of microcystin-LR in the presence of 1% (w/v TiO_2) Photospheres™(♦); Degussa P25 (▪).Error bars=1 SD; n=2.

Fig. 3 Degradation of microcystin-LR using UV-LEDs as source of radiation in the presence of 1% (w/v TiO_2) Photospheres™(♦); Degussa P25 (▪). Error bars=1 SD; n=2.

Fig. 4 (A) The effect of different catalyst loads (0.2 %(♦); 0.4 % (▪); 0.6 %(▲); 0.8 % (□);1.0 % TiO_2 (•) of Photospheres™ on the photocatalytic decomposition of microcystin-LR. (B) Dark adsorption of microcystin-LR to Photospheres™ at different catalyst loads. Error bars=1 SD; n=2.

Table 1 Properties and SEM observation of Degussa P25 (bar = 1 µm) and Photospheres™ (bar = 10 µm) [data from references 10, 15 and the present study]

Table 2 Summary of the degradation and dark adsorption of 11 different microcystin variants and nodularin with Photospheres™.
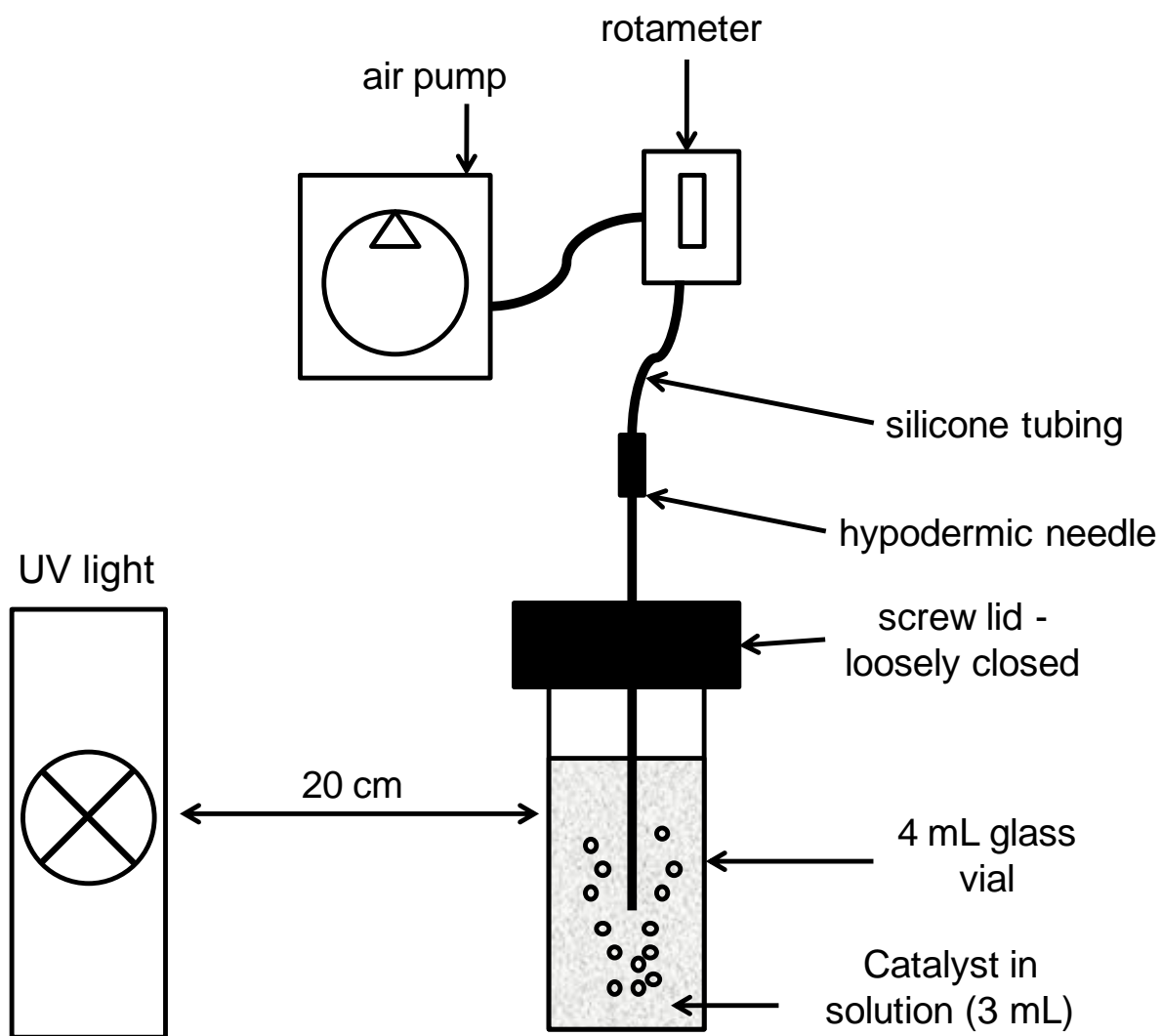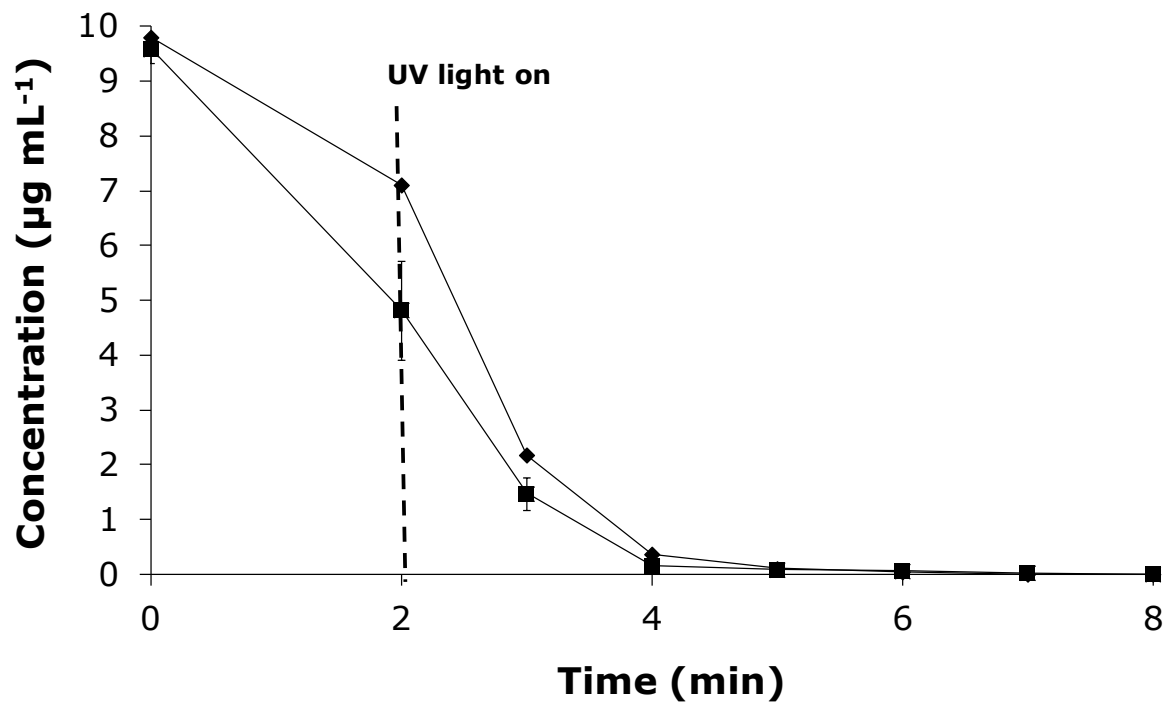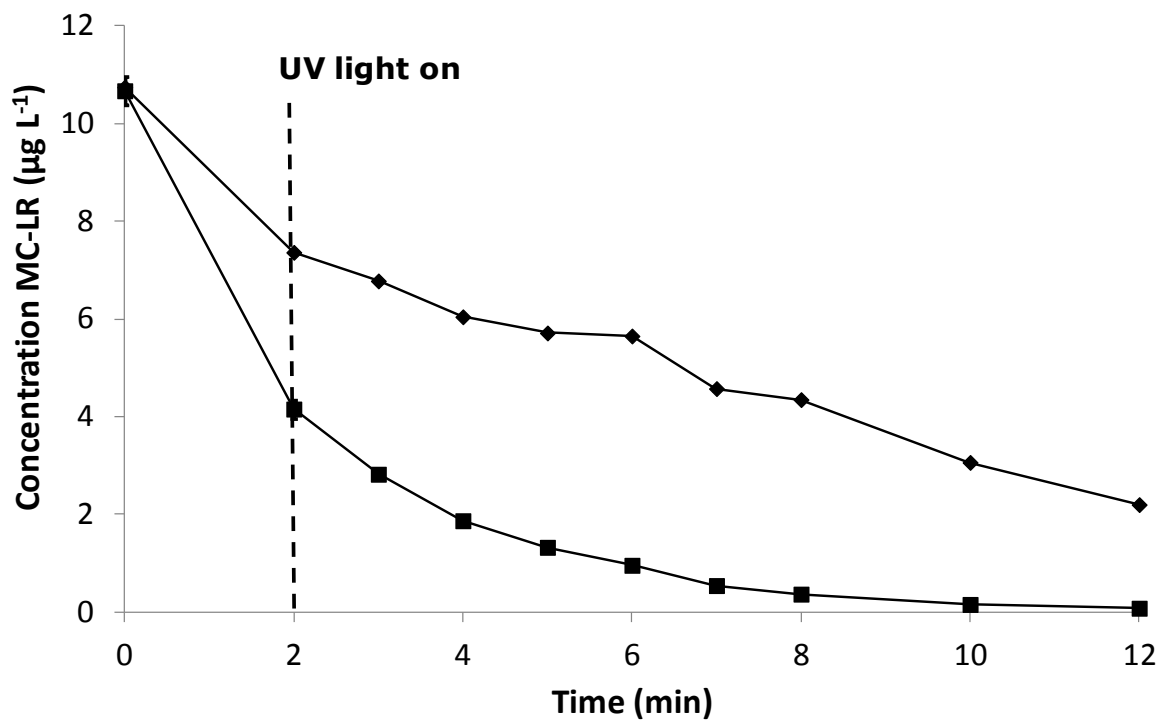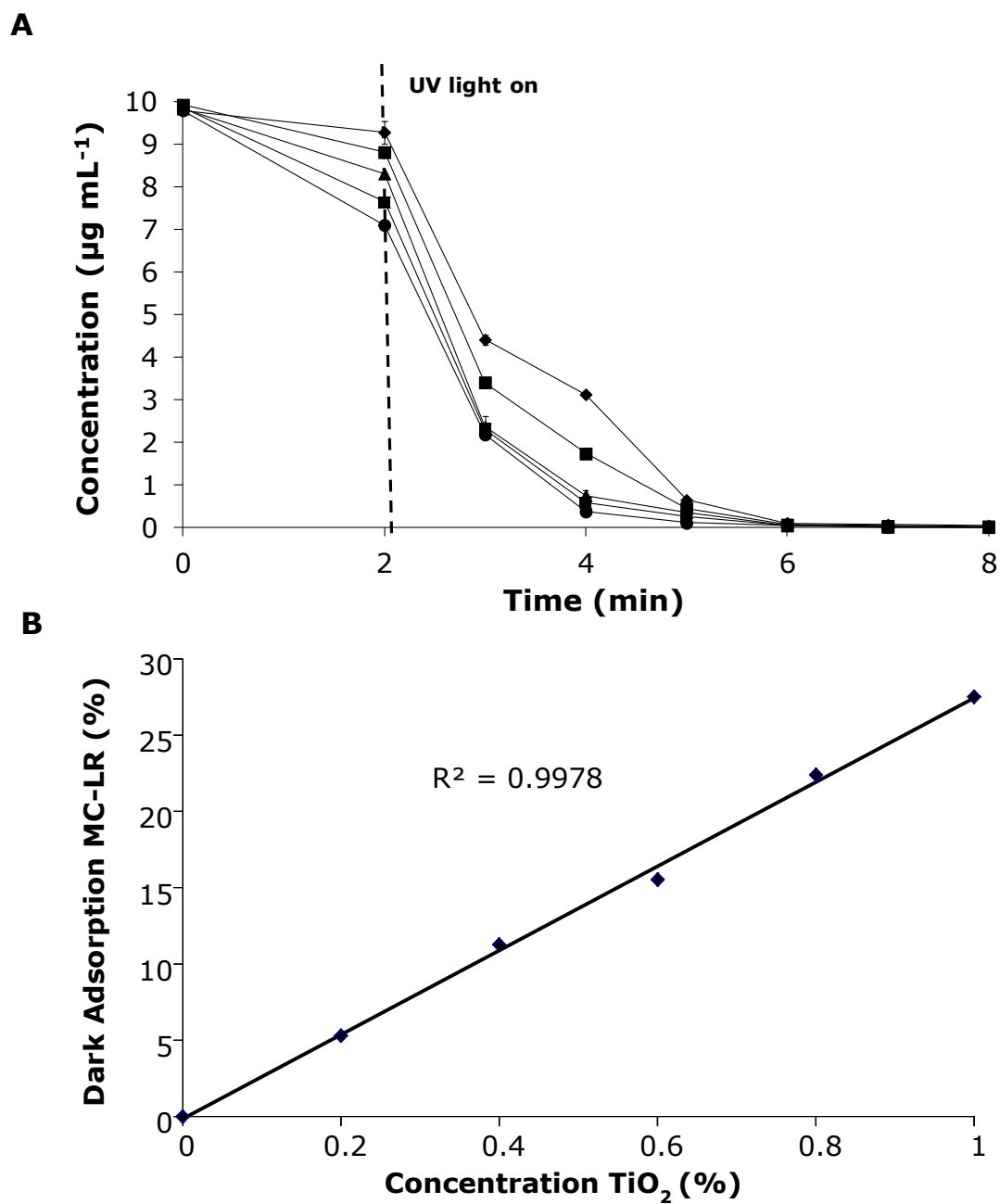
Fig 1.

Fig 2.

Fig. 3

A

B
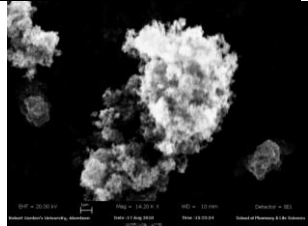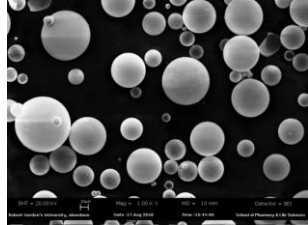
Fig 4.

Material	Properties	Image
Degussa P25	Nanoparticulate powder 100% TiO_2 BET surface area: 50 m^2 g^{-1} Particle size approx 25 nm TiO_2 composition: 75% anatase	
Photospheres™	Coated silica beads 17% TiO_2 BET surface area: 27 m^2 g^{-1} Particle size 40 µm (10 - 60 µm) TiO_2 Composition: 100% anatase	

Table 1.

Microcystin Variant	Dark adsorption (%)	Complete degradation* (min)
Nodularin	14	4
Microcystin-RR	21	3
Microcystin-LR	27	5
Demethylated Microcystin-RR	32	4
Microcystin-LA	34	4
Microcystin-HtyR	43	5
Demethylated Microcystin-LR	44	5
Methylated Microcystin-LR	45	4
Microcystin-YR	46	4
Microcystin-LY	48	2
Microcystin-LW	64	2
Microcystin-LF	70	2

* Time at which no microcystin/nodularin could be detected by HPLC

Table 2.