Electronic Supplementary Material (ESI) for Environmental Science: Water Research & Technology. This journal is © The Royal Society of Chemistry 2019

# 1

#### **Electronic Supplementary Information**

2

# 3 'All in one' photo-reactor pod containing TiO<sub>2</sub> coated glass beads and

## 4 LEDs for continuous photocatalytic destruction of cyanotoxins in water

5 H. Q. Nimal Gunaratne, Carlos J. Pestana, Nathan Skillen, Jianing Hui, S. Saravanan, Christine

6 Edwards, John. T. S. Irvine,\* Peter. K. J. Robertson,\* and Linda A. Lawton,\*

#### 7 Materials:

8 Porous glass beads in diameter of 2~4 mm (Poraver, Germany) were employed as 9 substrate in this work. The average density of the glass beads is around 0.6 g cm<sup>-3</sup>. 10 Titanium (IV) isopropoxide (Sigma-Aldrich, 97%) was used as precursor for TiO<sub>2</sub>. All 11 model compounds, methyl orange, phenol red and sorbic acid used in the 12 photodegradation study were purchased from Sigma-Aldrich. LED strips were 13 purchased from LightingWill company with specifications of 24W 365 nm-370 nm UV 14 (Ultraviolet).

15 The supports used for immobilising TiO2 were obtained from different commercial16 sources, as given below:

17 (1) Glass wool: Pyrex glass wool from Sigma-Aldrich

(2) Glass tape: Woven Glass Tape 1" Wide x 1/32" thick, manufactured by Wale
 Apparatus and supplied by GPE Scientific Limited.

20 Both glass wool and glass tape were thermally pre-treated at 500 °C to burn off any

21 extraneous organic matter that may be present before subjecting to coating.

22

### 23 Experimentation with dyes and sorbic acid

24

25 General procedures:

26 Stock solutions of Phenol red, methyl orange and sorbic acid in double distilled water 27 were made so that the optical densities of the highest absorbing bands were 28 approximately 0.8. Then, 300 cm<sup>3</sup> of these solutions were used for photodegradation 29 experiments where the photo-reactor pods were immersed in the solutions and

- 30 subsequently irradiated. Samples were withdrawn at prescribed time intervals and
  31 UV-Vis spectra were run on an Agilent UV-Visible spectrometer (model: UV-Vis-5000).
  32 The degradations were monitored by the disappearance of the main bands with time.
- 33
- 34



#### 35 Experiments with TiO<sub>2</sub> coated glass beads and dyes





38











45 Figure S3: Photocatalytic degradation of sorbic acid withTiO<sub>2</sub> coated glass wool, carried out
46 under neutral conditions(pH = 7.2)

47

#### 48 Preparation of TiO<sub>2</sub> coated glass beads:

49 An infiltration method was employed to coat TiO<sub>2</sub> onto the porous glass beads. To 50 avoid catalyst shedding caused from glass beads breakage, the porous glass beads 51 were washed in acetone with ultrasonic treatment for 30 minutes. After that, a two-52 hour calcination cycle at 550 °C was carried out to remove organic contamination on 53 the glass bead surface.

The precursor solution was prepared by adding 3.8 mL titanium (IV) isopropoxide into 10 mL isopropanol (Alfa Aesar, 99+%). After stirring for 30 minutes, the porous glass beads were immersed into the precursor solution for 5 minutes. Infiltrated glass beads were then dried in an oven at 80 °C. To increase the loading amount of the catalyst, a repeated infiltration process was performed. After another drying step (80 °C), the coated beads were calcined in a muffle furnace at 550 °C for 2 h to facilitate the formation of anatase phase. The loading amount of TiO<sub>2</sub> is approximately 32 wt% after 61 two coating processes.

#### 62 Characterisation:

63 The morphologies of uncoated and coated glass beads were observed by scanning 64 electron microscope (SEM, FEI Scios DualBeam) (Figure S4). Elemental analysis was 65 carried out on the same microscope working in energy dispersive X-ray spectroscopy

66 (EDX) mode.





Figure S4: SEM images of uncoated glass beads: surface morphologies in low (A) and high (B) magnifications; cross-section morphologies in low (C) and high (D) magnifications. Notes: Figure D is a backscattering image, which shows bright contrast of a glass bead. The dark contrast in some pores originates from resin used in sample preparation. It indicates that only parts of the pores are open so that the liquid resin can penetrate to fill.

74

75 Descriptions: The porous glass beads have many pores with varying sizes. Most of the 76 pores are closed inside the bulk where solution cannot reach. This was illustrated by 77 backscattering image in Figure S4(D). However, those closed pores contribute to the 78 buoyancy of the glass beads.

- 79
- 80
- 81

82

#### 83 Coating of glass wool and glass tapes

84 A measured quantity of glass wool (10 g) and glass tape (10 g) were dip coated once 85 using a sol-gel solution of TiO<sub>2</sub> made using a standard method starting with Ti(OiPr)<sub>4</sub>. 86 Excess sol-gel solution was drained off, dried on filter paper and air dried in a fume hood overnight. Then both materials were calcined at 550 °C for 2 h to maximise the 87 anatase phase formation. The TiO<sub>2</sub> loading was calculated taking into consideration 88 89 the weight difference observed after coating. Glass tape contained 8.5 % w/w of TiO<sub>2</sub> 90 while glass wool carried 7.2 % w/w. After calcination both materials were stored in a CaCl<sub>2</sub> desiccator. 91

92

#### **Construction of photoreactor pods** 93

94 The reactor pods were made from a fibre glass mesh with 4 mm x 4 mm holes attaching two LED strips (see Figure S5) to the inner wall with a silicone sealant. All the 95 edges were sewn together with glass fibre thread. The unit was powered by a 12 DC 96 97 V power supply.



98

- Figure S5: Photograph of a LED strip used in this study. Forward voltage was 12 dcV and 100
- each pod typically has a current of 0.12 A, giving an overall power of 1.44 W (based on a 101
- 102 2-LED strip pod).

103

#### 104 HPLC analysis of MC-LR

HPLC analysis was performed by using a Waters 2695 Separation Module. High 105 resolution photodiode array detection was performed with a Waters 2996 Photodiode 106 Array Detector (PDA). Separation of analytes was performed with a Symetry C18 107 column 2.1 mm (inner diameter) x 150 mm with a 5  $\mu$ m particle size (all Waters, UK). 108 The mobile phases used were ultrapure water and acetonitrile, both 0.05% TFA. 109 110 Chromatography was achieved with a linear gradient from 15 to 75% acetonitrile over 10 minutes, followed by a solvent wash and equilibration. Column temperature was 111 set to 40°C and the flowrate applied was 0.3 mL min<sup>-1</sup>. The resolution of the PDA was 112 set to 1.2 nm and data was acquired over a range of 200 to 400 nm. 113

114

115