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1 **Abstract**

2 Photocatalysis has been extensively studied in recent years for environmental wastewater
3 treatment applications. Although promising, it has yet to be globally adopted, as it faces many
4 challenges; namely cost, complexity and efficiency. This present work focuses on the
5 optimisation of a bespoke photocatalytic water treatment reactor. Contrary to other studies,
6 the reactor was exclusively built from inexpensive and readily available consumer market
7 parts, to facilitate a widespread adoption of this water treatment method. Photocatalytic TiO₂
8 was synthesised and immobilised on stainless steel woven mesh in a one-step process, via
9 reactive pulsed DC magnetron sputtering. A two-levels augmented screening design template
10 was used to optimise the performance of the bespoke photocatalytic reactor, consisting of 20
11 experimental runs. Five independent variables were studied, UV light intensity, number of
12 TiO₂-coated mesh layers, coating thickness, water flowrate and initial dye concentration.
13 Methylene blue dye solution was used as a model pollutant and the removal percentage after
14 5 h was used as a response. A linear regression model was built from the experimental results
15 and revealed that all first-order terms, with the exception of flowrate, were significant
16 contributors to the model pollutant removal. Increasing the coating thickness and the number
17 of TiO₂-coated mesh layers did improve the removal rate of methylene blue. These benefits
18 cancelled each other when both variables were at their highest levels, due to a decreased light
19 permeability through the mesh. ANOVA, lack-of-fit, and R² analysis confirmed the
20 significance of the linear regression model. Optimised conditions were identified, leading to
21 the removal of more than 90 % of the model pollutant after 5 h of UV-A illumination. The
22 calculated pseudo-first-order constant was as high as $14.5 \times 10^{-5} \text{ s}^{-1}$, while the quantum yield
23 was estimated to be 4.22×10^{-6} molecules/photons and the figure of merit was calculated at

24 1.14. This substrate/catalyst combination proved to be effective at degrading methylene blue,
25 with no evident performance degradation after 10 repeated cycles, equivalent to 360 h of
26 consecutive use. This present work demonstrates that it is possible to build an efficient
27 photocatalytic reactor from inexpensive computer enthusiast parts, combined with a highly
28 scalable and industry friendly photocatalyst production technique.

29 **Keywords:** Photocatalysis; water treatment reactor; titanium dioxide; magnetron sputtering;
30 design of experiments; stainless steel mesh.

31 **Highlights**

- 32 • TiO₂ coatings were deposited by magnetron sputtering onto steel mesh;
- 33 • Coatings were crystalline without further thermal treatment applied;
- 34 • Low-cost water treatment reactor was constructed from consumer market parts.
- 35 • Influence of variable parameters was studied for optimisation of reactor performance;
- 36 • Photocatalytic efficiency remained stable over 10 consecutive cycles of use.

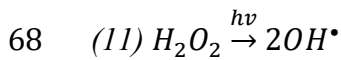
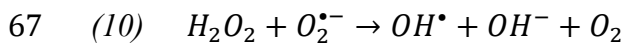
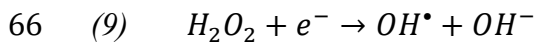
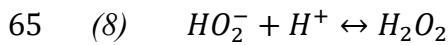
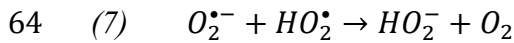
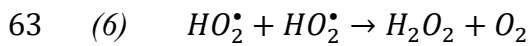
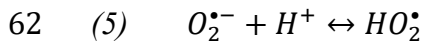
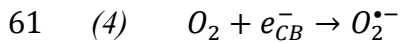
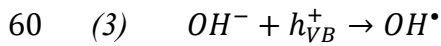
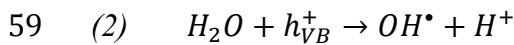
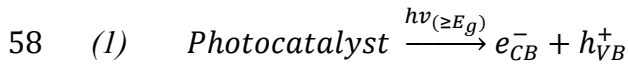
37

38 **1. Introduction**

39 According to the data published by the World Health Organisation (WHO), in 2017 almost
40 a third of the global population did not have access to safely managed, available and
41 uncontaminated drinking-water services (World Health Organization, 2019). It is predicted
42 that by 2025, half of the world's population will be living in water stressed areas. Use and
43 consumption of unsanitary water is known to result in rapid spread of diarrhoea, cholera,

44 dysentery, typhoid, and polio; thriving and praying on the most vulnerable populations. In
 45 the near future, water scarcity and imbalance is predicted to be one of the many consequences
 46 of climate change (Anser et al., 2020; Zhao et al., 2019; Zhu et al., 2020).

47 To address this pressing issue, environmentally friendly and sustainable processes must be
 48 developed and implemented to treat unsanitary water. Photocatalysis could be the answer, as
 49 it only requires a photocatalyst and an appropriate light source to operate. This advanced
 50 oxidation process (AOP) involves the absorption of photons of sufficient energy, by a
 51 semiconductor photocatalyst, to promote valence band electrons to the conduction band and
 52 form electron-hole pairs (equation (1)). These charge carriers diffuse to the photocatalyst's
 53 surface, react with water and oxygen molecules to form highly reactive radical species,
 54 through a series of chain reactions, as described by equation (2), (3), (4), (5), (6), (7), (8), (9),
 55 (10) and (11) (Fatima et al., 2019). These radical species progressively oxidise organic
 56 pollutants into less harmful intermediate products, until complete mineralisation is achieved
 57 (equation (12)).



69 (12) $\text{Pollutant} + \text{OH}^\bullet \rightarrow \text{intermediate} \rightarrow \text{CO}_2 + \text{H}_2\text{O}$

70

71 The most widely used photocatalyst is crystalline titanium dioxide (TiO_2), whose
72 photocatalytic properties were discovered by Fujishima and Honda in 1969 (Fujishima and
73 Honda, 1972). It is non-toxic, stable, inexpensive and has been extensively used for water
74 electrolysis, dye-sensitised solar cells, air/water purification, self-cleaning coatings, self-
75 cleaning glass, self-sterilising coatings, etc. (Byrne et al., 2018). Photocatalysts are most
76 commonly studied in powder form, where they generally possess higher activity than thin
77 films, but they then require post-treatment separation to safely discharge the treated water.
78 This major drawback limits the scalability and widespread adoption of powder-based
79 photocatalytic water treatment systems. Efforts were made to use immobilised
80 photocatalysts, as they do not require any post-treatment separation, but their effectiveness
81 can be limited by mass and photon transfer. These limitations can be mitigated when catalyst
82 thickness, reactant proximity, catalyst surface area and light permeability are considered
83 carefully (Sundar and Kanmani, 2020).

84 In his critical review, Juan José Rueda-Marquez identified several barriers, which hinder the
85 development of real world photocatalytic water treatment applications (Rueda-Marquez et
86 al., 2020):

- 87 • Most studies are performed on a laboratory scale.
- 88 • There is a lack of attention given to photocatalyst reusability.
- 89 • More than 60% of studies are performed on powders.
- 90 • Upfront and operational water treatment cost are rarely included.

91 This study aims at addressing some of the points raised by Rueda-Marquez et al., by building
92 and optimising a photocatalytic reactor, made with inexpensive components and loaded with
93 stainless steel mesh coated with TiO₂ thin films. The upfront and operating cost of this proof
94 of concept were both included in this study, while the reusability was assessed for 360 h of
95 consecutive use.

96 Practical use of photocatalytic materials for water and wastewater treatment can be facilitated
97 through their integration into so-called photocatalytic reactors. Although there is a wide
98 variety of reactor types (fluidized bed, optical fibre monolith, micro-channel, annular etc.),
99 they usually share common features, such as the presence of a reactor vessel, a light source,
100 a photocatalyst and a form of solution agitator. Photocatalytic reactors aimed towards
101 wastewater treatment can generally be classified in two categories: slurry type and
102 immobilised type. Regardless of the chosen type, the main attributes of an ideal
103 photocatalytic reactor should be the following (Colmenares and Xu, 2016): high quantum
104 efficiency, high catalyst specific surface area, efficient mass transfer, low cost and low
105 toxicity. To enable efficient transfer from a laboratory environment to real-world
106 applications, the photocatalyst manufacturing process should be scalable and the reactor
107 components should be inexpensive.

108 It is common practice for free form photocatalysts to be immobilised by spray coating (Cortes
109 et al., 2019; Lasa et al., 2005), which involves slurry preparation, air spraying and calcination
110 steps. In an earlier study, 304 stainless steel mesh was successfully coated with photocatalytic
111 TiO₂, in a one-step process, demonstrated its efficiency against a range of model pollutants
112 and identified $O_2^{\bullet-}$ and OH^{\bullet} as the photocatalytic reaction's main driving force (Grao et al.,
113 2020). The photocatalyst was deposited by reactive magnetron sputtering, in a one-step

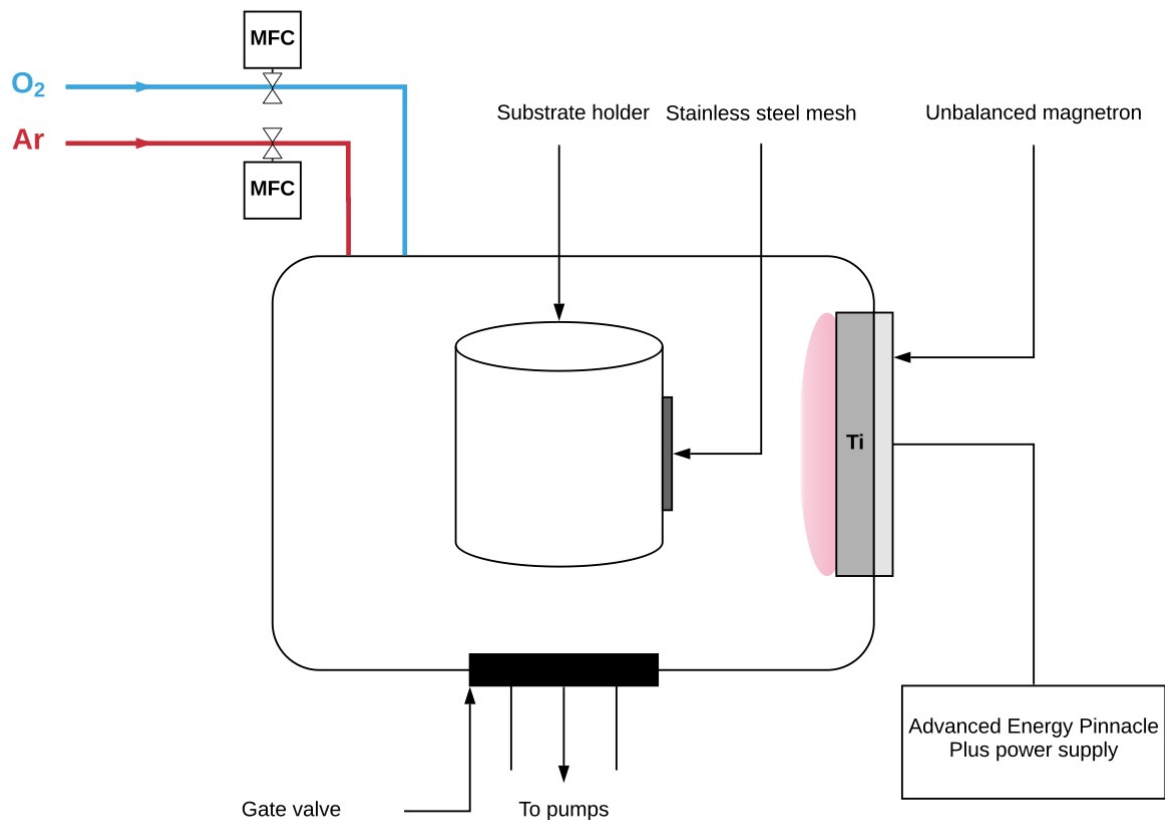
114 process, which represents a significant time and economic gain, especially for high volume
115 manufacturing, compared to multi-step chemical techniques. Magnetron sputtering is
116 reproducible, highly scalable and provides excellent control over chemical and
117 morphological properties (Kelly and Arnell, 2000). This stainless-steel mesh substrate was
118 chosen for its inexpensiveness, flexibility, durability and, importantly, ability to let light pass
119 through. Layers of stainless-steel woven mesh can be stacked in a photocatalytic reactor,
120 increasing the catalyst load whilst maintaining light permeability. TiO₂ coated stainless steel
121 mesh was integrated in a bespoke photocatalytic reactor, LCPR-I (Low-Cost Photocatalytic
122 Reactor-I). Key parameters were optimised to maximise the reactor's efficiency, based on its
123 ability to degrade a model pollutant; methylene blue (MB). Five parameters were varied
124 along an augmented screening design template to identify the most important parameters and
125 optimise the process: UV-A light intensity, number of TiO₂-coated mesh layers, coating
126 thickness, water flowrate and initial dye concentration.

127 This reactor fabrication process did not involve any expensive components (glass, quartz,
128 membranes, air injector etc.) and it was almost exclusively built from components available
129 in an everyday computer store, making this system easily accessible and affordable. The
130 photocatalyst deposition process is scalable, reproducible and already widely established in
131 high volume manufacturing processes. The combined affordability, simplicity and efficiency
132 of this proof of concept represents a sustainable option to treat wastewater and help to bridge
133 the gap between materials research and real-world applications.

134 **2. Materials and Methods**

135 **2.1. Deposition process**

136 Titanium dioxide thin films were deposited in a single-stage process in a Nordiko sputtering
137 rig (Fig. 1), under a high vacuum, achieved through a combination of rotary (BOC Edwards
138 80) and turbo molecular (Leybold TMP1000) pumps. A single directly cooled 300x100 mm
139 titanium target (99.5% purity) was fitted onto a Gencoa Ltd unbalanced type II magnetron.
140 The distance between the target and the substrate was kept at 50 mm for all deposition runs.
141 The argon flow rate was kept constant at 50 sccm for all deposition runs. The oxygen flow
142 was regulated by a Speedflo®™ controller from Gencoa Ltd., to produce stoichiometric TiO₂
143 films and to minimise target poisoning. The magnetron was powered by an Advanced Energy
144 Pinnacle Plus power supply in pulsed DC mode operating at a power of 2 kW, frequency of
145 100 kHz and 60% duty. The coatings were deposited for either 1 or 2 h onto 15 × 12.5 and
146 15 × 9 cm² sheets of stainless steel 304 mesh, with a 0.223 mm aperture and a wire diameter
147 of 0.14 mm (purchased from the Mesh Company, Warrington, UK); the substrate was
148 ultrasonically pre-cleaned in acetone prior to deposition. All chemicals used were purchased
149 from Sigma Aldrich, unless stated otherwise.



150

151 *Figure 1. Schematic representation of the Nordiko sputtering rig.*

152 2.2.Characterisation

153 The thin film morphology was evaluated by scanning electron microscopy (SEM) using a
 154 Zeiss Supra 40 VP-FEG-SEM. The deposited film thicknesses were estimated from their
 155 cross-sectional SEM micrographs. The crystallinity of the coatings was assessed by X-ray
 156 diffraction (XRD), on a Panalytical Xpert system, with $CuK_{\alpha 1}$ radiation at 0.154 nm, in
 157 grazing incidence mode at 3° angle of incidence over a scan range from 20 to 70° (2θ), the
 158 accelerating voltage and applied current were 40 kV and 30 mA, respectively. The optical
 159 band gap of the TiO_2 coatings on mesh substrates was estimated using the Tauc plot method
 160 (Tauc et al., 1966), by measuring the optical absorbance of TiO_2 coatings on soda lime glass

161 slides produced under the same conditions. The absorbance spectrum and corresponding
162 Tauc plot are given in supplementary materials (S1).

163 2.3. Photocatalytic performance assessment

164 The photocatalytic performances of the bespoke water treatment reactor were assessed by
165 monitoring its ability to degrade methylene blue under UV-A light. The reactor was loaded
166 with TiO₂ coated mesh and filled with an aqueous methylene blue (purchased from Alfa
167 Aesar) solution of 500 mL at a concentration of either 1 or 5 $\mu\text{mol.L}^{-1}$. The reactor was left
168 in the dark at room temperature for 12 h under continuous solution circulation to reach
169 adsorption-desorption equilibrium. Once reached, the UV-A source (Sankyo Denki BLB
170 lamps, peak output at 365 nm) was powered up for 24 h. The methylene blue main absorption
171 peak at 664 nm was monitored every 1 h with an Ocean Optics USB4000 UV-visible
172 spectrometer. Between each test, both the coated mesh sheets and the reactor were thoroughly
173 rinsed with distilled water. The reactor's photocatalytic degradation efficiency was
174 calculated using equation (13) and used as a response to optimise the photocatalytic
175 degradation process, with A_0 and A_t as MB's main absorbance peak at 0 and 5 h of UV
176 irradiation, respectively. The pseudo-first-order rate constant (k_α), quantum yield (QY) and
177 figure of merit (FOM) were calculated as performance metrics for the best photocatalytic
178 reactor configuration (run No. 16). The pseudo-first-order rate was obtained by plotting
179 $\ln(A_0/A_t)$ against time and calculating the plot's gradient. QY is used as a metric to quantify
180 how effectively a semiconductor can utilise absorbed photons to decompose a pollutant, it
181 was obtained using equation (14), with r ($\text{mol.cm}^{-2}.\text{s}^{-1}$) the reaction rate and φ ($\text{mol.cm}^{-2}.\text{s}^{-1}$)
182 the flux of absorbed photons (He et al., 2020). The figure of merit is a performance indicator
183 which takes into account the volume of treated solution, the amount of catalyst, the treatment

184 time and the energy consumption of the system. FOM was calculated using equation (15) and
185 graded between 0 and 100 using a conversion factor used to index 85 different photocatalytic
186 systems (Anwer et al., 2019).

$$187 \quad (13) \quad MB \text{ removal } (\%) = \frac{A_0 - A_t}{A_0} \times 100$$

$$188 \quad (14) \quad QY = \frac{\text{number of reacted molecules}}{\text{number of absorbed photons}} = \frac{r}{\phi}$$

$$189 \quad (15) \quad FOM = \frac{\text{Product obtained (L)}}{\text{Catalyst dosage (g.L}^{-1}) \times \text{Time (h)} \times \text{Energy consumption (Wh.}\mu\text{mol}^{-1})}$$

190

191 The photon flux was obtained by integrated irradiance measurement, from 300 to 410 nm,
192 with a USB4000 UV-visible spectrometer from Ocean Optics. Due to the photocatalyst's
193 wide bandgap (3.2 eV), it is assumed that wavelengths over 410 nm cannot excite electrons
194 from the valence to the conduction band. To obtain an estimation of the number of absorbed
195 photons, irradiance measurements were performed by drilling a hole in the middle of the
196 reactor and inserting the optic fibre in the MB filled reactor after 2.5 h of reaction, with and
197 without the coated mesh. The irradiance measurement spectra are provided in supplementary
198 materials (S2).

199 2.4. Durability and reusability assessment

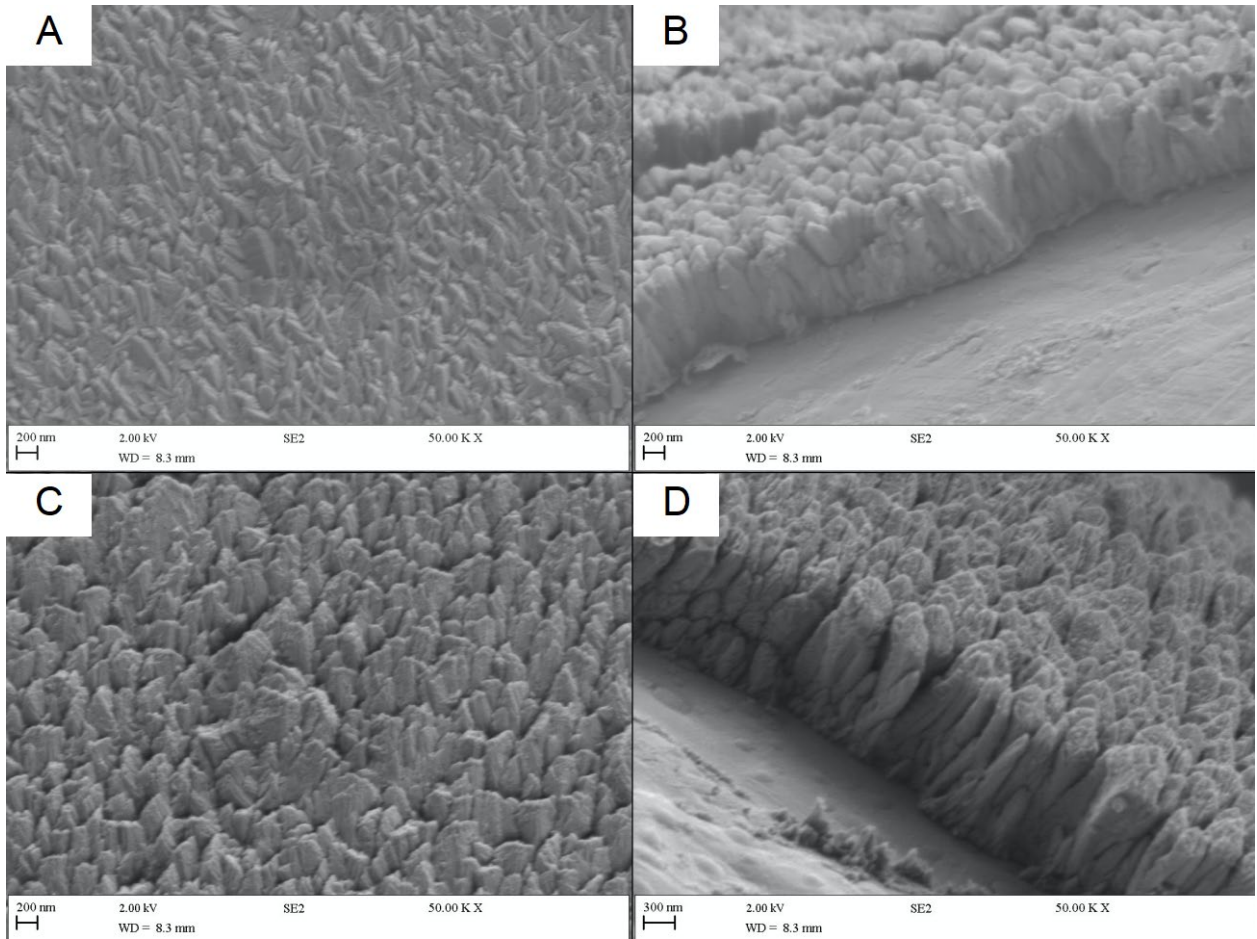
200 To evaluate the durability and reusability of the coated mesh, 10 consecutive MB removal
201 tests were performed with the most efficient configuration (run No. 16), using the same
202 photocatalytic activity assessment apparatus. A small square of 0.25 cm² was cut from the
203 coated mesh sample, to verify the thin film's integrity by Raman mapping analysis.
204 Afterwards, the sample was soldered back to its original position, for further testing and the

205 operation was repeated 2 additional times. Raman mapping was performed after the 1st, 5th
206 and 10th tests using a DXR Raman microscope from Thermo Scientific. The Raman spectra
207 were analysed over a range of 100 – 1000 cm⁻¹ and the Raman maps were constructed using
208 the integrated intensities of the main anatase peak at 144 cm⁻¹ (Ohsaka et al., 1978). The laser
209 was operated at a wavelength of 532 nm, with a power of 10 mW, 900 lines per mm grating,
210 a long working distance (LWD) microscope objective with magnification of ×50, an
211 estimated spot size of 1.1 μm and a 25 μm pinhole. 10201 Raman spectra were acquired per
212 analysis, using a step size of 50 μm along the Y and X axes.

213 3. Results

214 3.1. Coating deposition and characterisation

215 Stainless steel 304 woven mesh was coated with TiO₂ by pulsed DC reactive magnetron
216 sputtering in a single-step process at ambient temperature. To evaluate the impact of coating
217 thickness on the reactor's photocatalytic capabilities, two deposition times were used, 1 and
218 2 h. Table 1 summarises the conditions used to obtain these two types of coatings and their
219 respective characteristics. The coatings obtained at the two deposition times were examined
220 by FEG-SEM and their top view and cross-sectional micrographs are given in Fig. 2. The top
221 view of the two conditions revealed a dense microstructure with crystal-like features, as
222 shown in Fig. 2(A, C). An analysis of the samples' cross-section, in Fig. 2(B, D), highlighted
223 the columnar aspects of the coatings. This might be a result of the angled deposition of TiO₂
224 on the curved surface of the stainless-steel substrate, which could promote columnar growth
225 through shadowing effects. Average thicknesses of 1.1 ± 0.1 and 1.6 ± 0.1 μm were
226 measured for the 1 and 2 h depositions, respectively.



227

228 *Figure 2. FEG-SEM micrographs of the TiO₂ coated mesh samples; (A) 1 h deposition top-*
 229 *view; (B) 1 h deposition cross-section; (C) 2 h deposition top-view; (D) 2 h deposition cross-*
 230 *section.*

231 *Table 1. Deposition conditions and characteristics of the two coating types.*

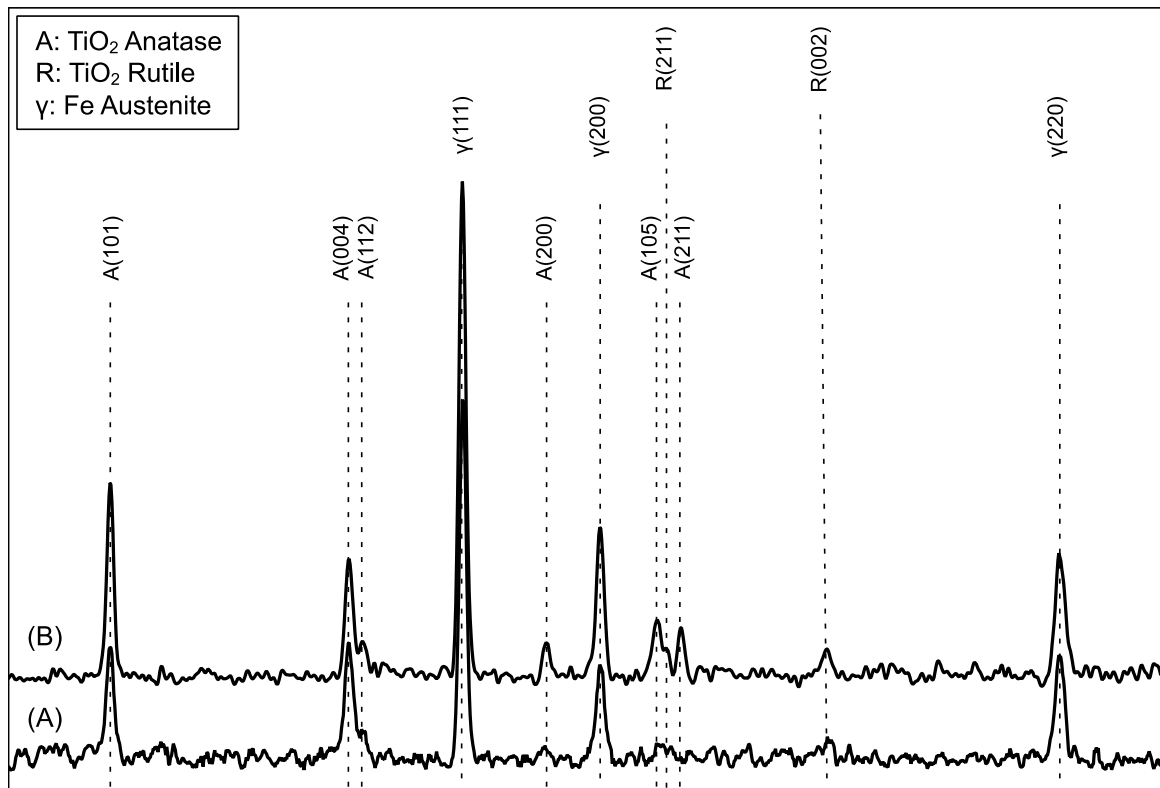
Deposition parameters	Condition 1	Condition 2	Units
Deposition time	1	2	h
Power	2	2	kW
Frequency	100	100	kHz
Base pressure	0.3	0.3	(10 ⁻²) Pa
Working pressure	44	44	(10 ⁻²) Pa

Gas	Ar/O ₂	Ar/O ₂	-
Distance _{target-substrate}	5	5	cm
Characterisation			
Crystalline phase(s)	Anatase	Anatase + Rutile	-
Thickness	1.1± 0.1	1.6± 0.1	µm

232

233 The XRD analysis of the TiO₂ coated mesh revealed the presence of well-defined diffraction
234 peaks, corresponding to crystalline TiO₂ for both deposition times (Fig. 3). Diffraction peaks
235 at 44.42° (111), 51.58° (200), 75.48° (220) were identified as austenite stainless steel using
236 the JCPDS card 00-003-0397, arising from the substrate material. The diffraction pattern of
237 the 1 h deposition (Fig. 3(A)) revealed anatase diffraction peaks at 25.35° (101), 37.93° (004)
238 and 38.61° (112) identified with the JCPDS card 96-720-6076. After 2 h of deposition (Fig.
239 3 (B)), anatase 25.35° (101), 37.93° (004), 38.61° (112), 48.10° (200), 53.89° (105), 55.29°
240 (211) and rutile diffraction peaks at 54.32° (211), 62.74° (002) were identified with the
241 JCPDS cards 96-720-6076 and 96-900-4145, respectively.

242 For both deposition times, crystalline titanium dioxide structures were obtained in a one-step
243 process without any thermal treatment. Increasing the coating's thickness gave rise to new
244 anatase diffraction peaks and to the appearance of an additional rutile phase. Anatase and
245 rutile mixtures are known to have an enhanced photocatalytic activity compared to each
246 polymorph on its own (Bickley et al., 1991). This rutile and anatase mixture could result in
247 an increase photocatalytic activity for the 2 h deposition samples.



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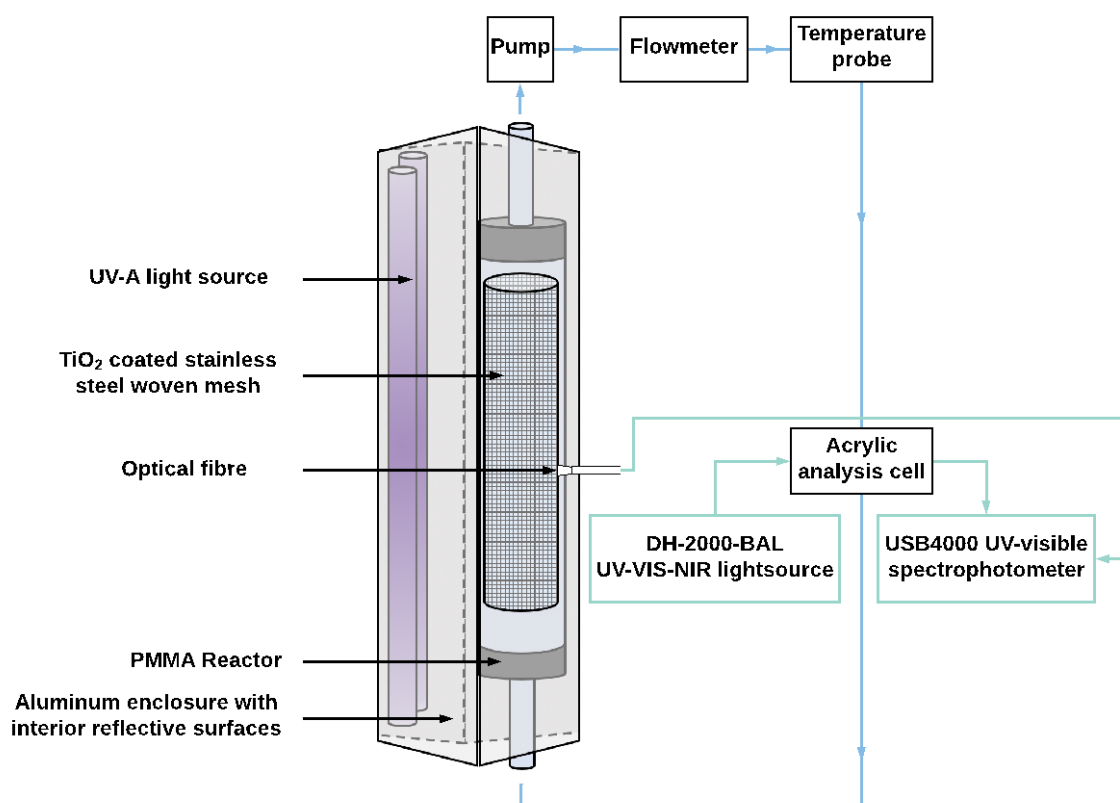
249 *Figure 3. XRD analysis of the TiO₂-coated mesh samples; (A) 1 h deposition; (B) 2 h*
 250 *deposition*

251 3.2. Photocatalytic reactor design

252 The LCPR-I design inspiration can be traced to the Photo-CREC-Water I, developed at the
 253 Chemical Reactor Engineering Centre (CREC) of the University of Western Ontario, by Lasa
 254 et al. (2005). Likewise, the catalyst was immobilised on stainless steel mesh, albeit using
 255 another immobilisation technique, and the reactor was operated in batch mode. Unlike Photo-
 256 CREC-Water I, this bespoke reactor utilises an external light source and does not involve
 257 quartz or glass components, significantly reducing the system's cost and increasing its

258 durability. With the exception of the UV-A lamps, the set-up was built exclusively from
259 affordable and readily available components, purchased from the computer enthusiast
260 market. Fig. 4 provides a schematic representation of the bespoke water treatment
261 photocatalytic reactor loaded with TiO_2 -coated stainless-steel mesh photocatalyst.

262



263

264 *Figure 4. Schematic representation of LCPR-I utilising TiO_2 -coated stainless-steel mesh.*

265 In brief, the system is comprised of a cylindrical reactor made from PMMA (OD: 5 cm, h:
266 24 cm), transparent PVC tubing (OD: 16 mm, ID: 10 mm), a 12 V pump, a flowmeter, a
267 temperature probe and an acrylic analysis cell. The reactor was placed in an aluminium
268 enclosure with a UV-A irradiation source, detailed in Section 2.3. Depending on the design
269 matrix experiment, either 1×15 W or 2×15 W light bulbs were used, the pump's voltage

270 was varied between 6 and 12 V to adjust the flowrate. The reactor was loaded with either
271 $15 \times 12.5 \text{ cm}^2$ or $15 \times 12.5 + 15 \times 9 \text{ cm}^2$ cylinder(s) of stainless steel 304 sheets of mesh,
272 coated on both sides with TiO_2 with varying thickness levels. A full breakdown of the upfront
273 price of the LCPR-I is given in supplementary data (S3).

274 3.3.Design of experiments

275 The independent variables used for this design of experiments array are presented in Table
276 2, including corresponding levels and coding. The augmented screening design was
277 constructed and analysed using the JMP 14 SW statistical software from SAS. The studied
278 variables were UV light intensity (W) (X_1), number of TiO_2 -coated mesh layers (X_2), coating
279 thickness (μm) (X_3), flow rate (L min^{-1}) (X_4), and initial dye concentration ($\mu\text{mol.L}^{-1}$) (X_5);
280 these variables were varied along two levels; low (-1) and high (+1); all variable parameters
281 were chosen to be within operational range of the proposed reactor and therefore, no design
282 modifications were required. Noise factors, namely, temperature (K) and power consumption
283 (W) were also recorded during each experiment. Although temperature is known to positively
284 influence photocatalytic reactions (Gupta et al., 2012; Hu et al., 2010; Yamamoto et al.,
285 2013); the measured variations were considered too low to have a significant impact (Table
286 3). Z. Shams-Ghahfarokhi et al. reported an increased decolorization efficiency at higher
287 temperatures, with significant improvements only occurring above 333K (Shams-
288 Ghahfarokhi and Nezamzadeh-Ejhih, 2015). The power drawn by the system was measured
289 directly at the wall with a wattmeter. Power consumption varied from 37 to 67 W, depending
290 on the levels of the independent operating variables (Table 3). The pH values of the media
291 were measured before and after each experiment; this value was 6, regardless of variable
292 experimental parameters, therefore, was not discussed further in work progression. To assess

293 the contribution of photolysis, a run termed No. 0 was performed with two sets of uncoated
 294 mesh, 1 $\mu\text{mol.L}^{-1}$ of initial dye concentration and 30 W UV light. Photolysis seemed to
 295 account for less than 10 % of the dye degradation after 5 h of UV irradiation.

296 *Table 2. Experimental ranges and levels of the independent operating variables.*

Variables	Symbol	Unit	Range and levels	
			-1	+1
UV light	X ₁	W	15	30
Number of TiO ₂ -coated mesh layers	X ₂	–	1	2
Coating thickness	X ₃	μm	1.1	1.6
Flowrate	X ₄	L.min ⁻¹	5.14	9.54
Initial dye concentration	X ₅	$\mu\text{mol.L}^{-1}$	1	5

Uncontrollable variables: Temperature (K) and Power consumption (W)

297

298 *Table 3. Design matrix for the 5 tested independent variables with the experimental and*
 299 *predicted responses.*

Run No.	X ₁	X ₂	X ₃	X ₄	X ₅	MB removal (%)		Uncontrollable variables	
						Experimental	Predicted	Temperature	Power
								(K)	drawn (W)
0	+1	-	-	-1	-1	9.9	-	299	53
1	+1	+1	-1	-1	+1	64.8	60.8	300	54
2	-1	-1	+1	+1	+1	45.2	43.8	300	50
3	-1	+1	-1	+1	+1	36.4	44.0	300	49
4	+1	-1	-1	-1	+1	37.6	44.3	300	53
5	-1	+1	+1	-1	-1	61.3	70.8	298	37

6	+1	-1	-1	+1	-1	72.4	72.6	303	67
7	-1	-1	-1	+1	-1	54.9	55.8	299	50
8	+1	+1	+1	+1	-1	82.5	87.6	303	67
9	+1	+1	+1	+1	+1	58.4	59.3	306	66
10	-1	+1	-1	-1	-1	73.2	72.3	300	37
11	+1	-1	+1	-1	-1	88.7	89.0	300	54
12	-1	-1	+1	-1	+1	37.0	43.8	298	38
13	+1	+1	-1	+1	+1	60.1	60.8	303	66
14	+1	-1	+1	-1	+1	70.3	60.6	300	53
15	-1	+1	+1	+1	-1	77.6	70.8	300	49
16	+1	+1	-1	-1	-1	93.0	89.2	300	54
17	-1	-1	-1	+1	+1	26.8	27.4	300	37
18	+1	-1	+1	+1	-1	85.2	89.0	302	67
19	-1	-1	-1	-1	-1	64.1	55.8	297	37
20	-1	+1	+1	-1	+1	52.1	42.4	296	38

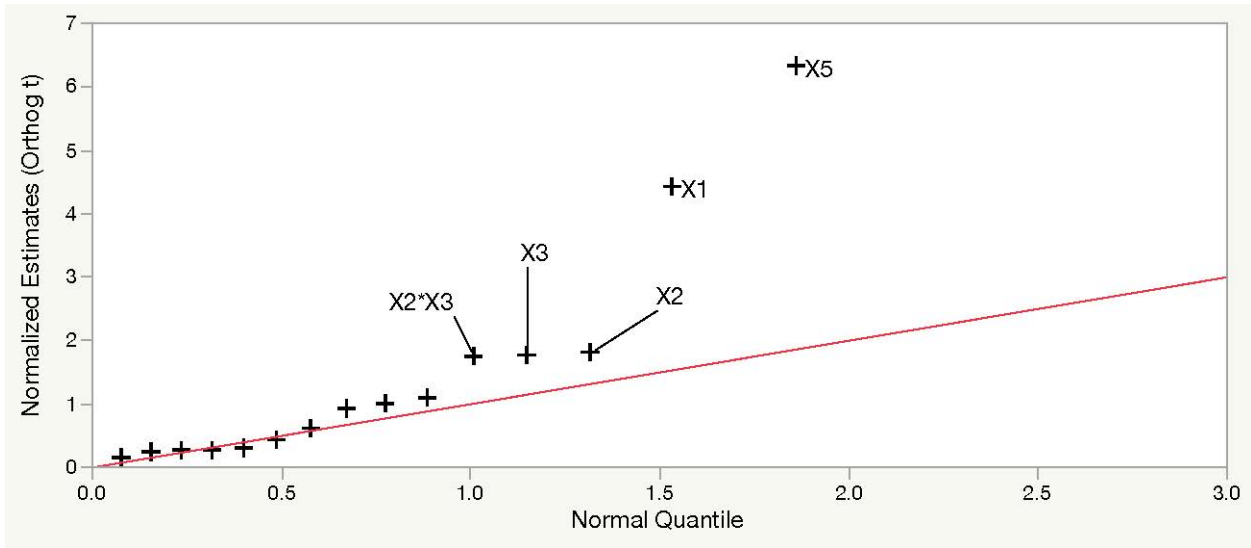
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301 The two-levels design matrix with the corresponding experimental and predicted results for
302 each statistical combination of independent variables are displayed in Table 3. The predicted
303 values were obtained by fitting a regression model to the experimental data, to determine the
304 optimal operating conditions. Regression coefficients were determined to develop a
305 regression model, based on significant main or interaction effects. In the case of a 2-levels
306 experiment, the regression coefficients are calculated by dividing the estimates of effects E_f
307 by 2. A regression model (16) can then be designed, with \hat{y} as the predicted response, β_0 as
308 the intercept, β_i as a regression coefficient, β_{ij} as the interaction between the process
309 parameters X_i and X_j , and ‘ ϵ ’ as the random error component.

310 (16) $\hat{y} = \beta_0 + \beta_1 X_1 + \beta_2 X_2 + \dots + \beta_{12} X_1 X_2 + \beta_{12} X_1 X_2 + \dots + \varepsilon$

311 Using a backward selection method, a regression model was generated with all factors and
312 2nd order interactions (Bruce and Bruce, 2017). Statistically significant independent variables
313 and 2nd order interactions were identified using a half-normal plot. This graphical tool uses
314 estimated effects to visually assess the significance of factor(s) and interaction(s) (Daniel,
315 1959). Insignificant factors or interactions should fall along a straight line, while significant
316 one's should form outliers. As displayed in Fig. 5, initial dye concentration (X_5), UV light
317 intensity (X_1), number of TiO₂-coated mesh layers (X_2), coating thickness (X_3) and the
318 interaction between coating thickness and number of TiO₂-coated mesh layers ($X_2 X_3$) seem
319 to stand out as significant. Flowrate does not seem to play any significant role in the MB
320 removal, suggesting that the lowest selected level is appropriate, and that mass transfer does
321 not bottleneck the reaction. The parameter estimates report (Table 4) presents the significance
322 and direction of the chosen parameters and interaction, with their associated t-ratios and p-
323 values. All selected parameters have an absolute t-ratio greater than 1.96 and p-values smaller
324 than 0.05, confirming the statistically significance of their effects.

325



326

327 *Figure 5. Half-normal plot for all independent variables and 2nd order interactions.*

328

329 *Table 4. Parameter estimates for significant independent variables and 2nd order*
 330 *interactions.*

Term	Estimate (%)	Std Error (%)	t-ratio	p-value
Intercept	62.0	1.5	42.3	<0.0001
X ₁	8.4	1.5	5.6	<0.0001
X ₂	3.8	1.5	2.6	0.0212
X ₃	3.7	1.5	2.5	0.0242
X ₅	-14.2	1.5	-9.5	<0.0001
X ₂ X ₃	-4.4	1.5	-2.9	0.0112

(X₁) UV light; (X₂) number of TiO₂-coated mesh layers; (X₃) Coating thickness; (X₄) Flowrate; (X₅) Initial dye concentration

331

332 Statistically non-significant predictors were successively taken away from the model until

333 only statistically significant ones remained. Using the parameter estimates, the following

334 regression model (17), was designed to predict MB removal percentage, after 5 h, by the
335 TiO₂-coated mesh reactor.

$$336 \quad (17) \quad \hat{y} = 62 + 8.4 \times X_1 + 3.8 \times X_2 + 3.7 \times X_3 - 14.2 \times X_5 - 4.4 \times X_2X_3$$

337 The quality of the fit for this model was assessed using an analysis of variance (ANOVA),
338 presented in Table 5. The F-ratio was used to assess whether the designed model differed
339 significantly from a model where all predicted values are equal to the response mean. If the
340 null hypothesis is true, the F-ratio should be close to 1, *i.e.* the chosen parameters do not
341 describe accurately the actual data variations (Dougherty, 2011; Nguyen et al., 2019). The
342 associated p-values measured the probability of obtaining a F-ratio, as large as the one
343 observed, with all parameters set to zero except the intercept. Small p-values (<0.05) would
344 indicate that the observed large F-ratio is unlikely to be obtained by pure chance alone and
345 that the null hypothesis can be rejected. The large F-ratio (28.895) and small p-value
346 (<0.0000), obtained with the ANOVA confirm that the model describes accurately the data
347 variations and that the chosen parameters are significant.

348 Besides, the accuracy of fit between the experimental values and the model was assessed by
349 analysing the lack-of-fit (LOF) (Nguyen et al., 2019). The regression model fits the
350 experimental data well, as the mean square of the lack-of-fit error (0.004) was close to the
351 pure error (0.005). The lack-of-fit for this model was statistically insignificant with a large
352 p-value (0.610) and a F-ratio close to 1 (0.850), confirming that this model can be used for
353 both prediction and optimisation.

354 The model's goodness-of-fit was confirmed by the R^2 (0.91) and R_{adjusted}^2 (0.88) for
355 experimental data points plotted against the predicted values (Montgomery, 2008). The
356 R_{adjusted}^2 is a modified version of R^2 which takes into account the model's number of

357 predictors. The small gap between R^2 (0.91) and R_{adjusted}^2 (0.88) indicates that the
 358 experimental data variations are in accordance with the model and that the predicted
 359 responses are trustworthy (Table 5). Plotting the data against the predicted responses (Fig.
 360 6(A)) highlighted the agreement of the model with the experimental values. The normal
 361 probability plot of the residuals, shown in Fig. 6(B), approximately forms a straight line,
 362 supporting the assumptions that the error terms are normally distributed.

363 Overall, the analysis of variance, lack of fit, and R^2 results all confirmed that the model was
 364 statistically significant and could be used to predict and optimise the % removal of MB after
 365 5 h using the TiO₂-coated mesh photocatalytic reactor.

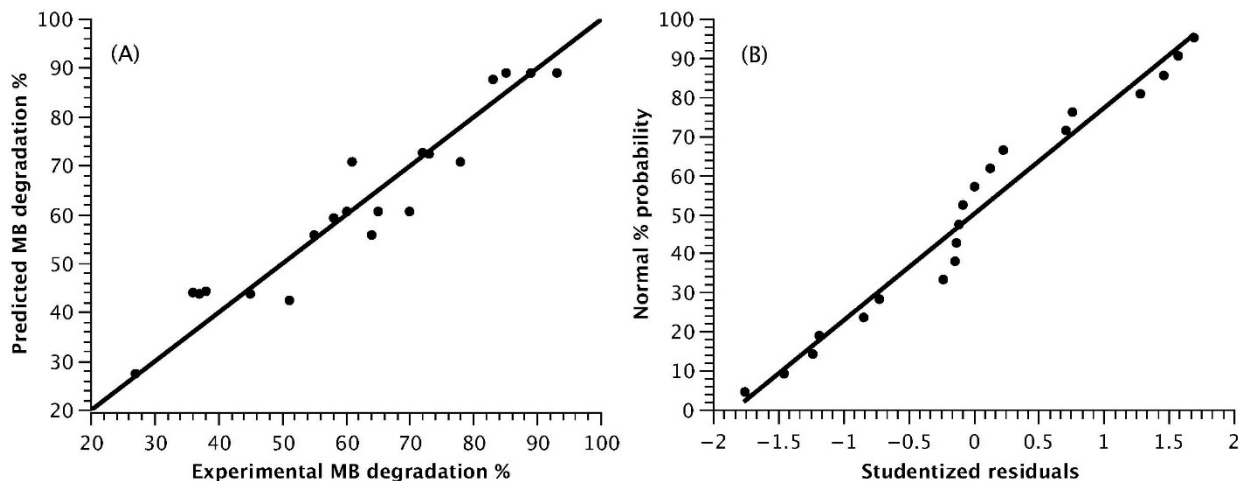
366

367 *Table 5. Analysis of variance (ANOVA) and Lack-of-fit (LOF) for MB removal efficiency of*
 368 *the TiO₂-coated stainless-steel mesh-based photoreactor.*

Source	DF	Sum of Squares	Mean Square	F Ratio	p-value
Model	5	0.620	0.124	28.895	<0.0000
Error	14	0.060	0.004		
C. Total	19	0.680			
Lack of fit	9	0.036	0.004	0.850	0.610
Pure error	5	0.024	0.005		
Total error	14	0.060			

$R_{\text{squared}} = 0.9117, \text{ Adjusted } R_{\text{squared}} = 0.8801$

369

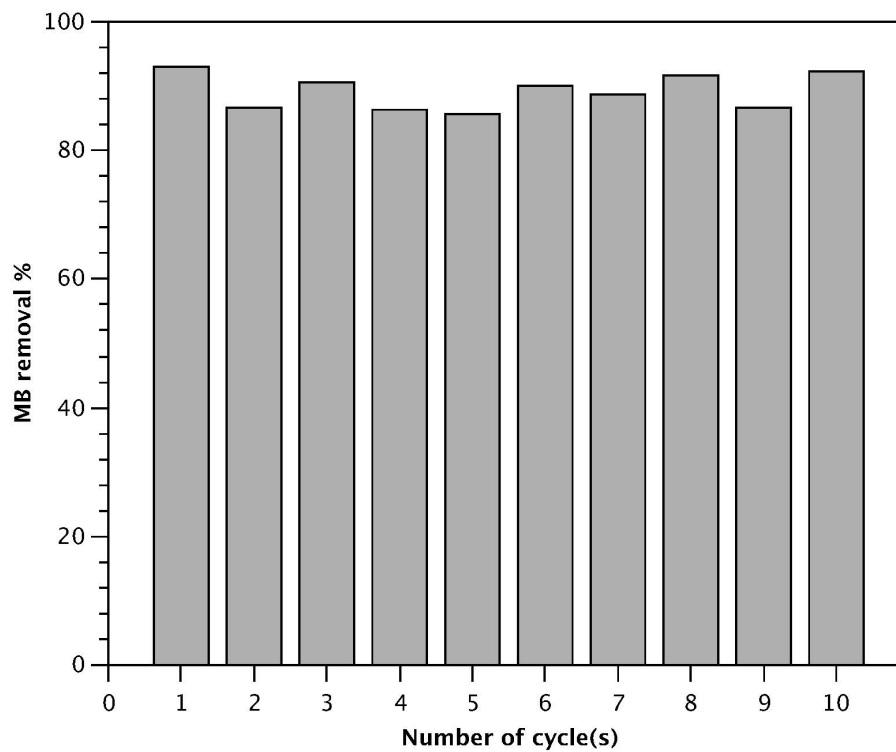


370

371 *Figure 6. Diagnostic plots for the photocatalytic MB removal % after 5 h: (A) Experimental*
 372 *by predicted plot; (B) Normal probability plot of residuals.*

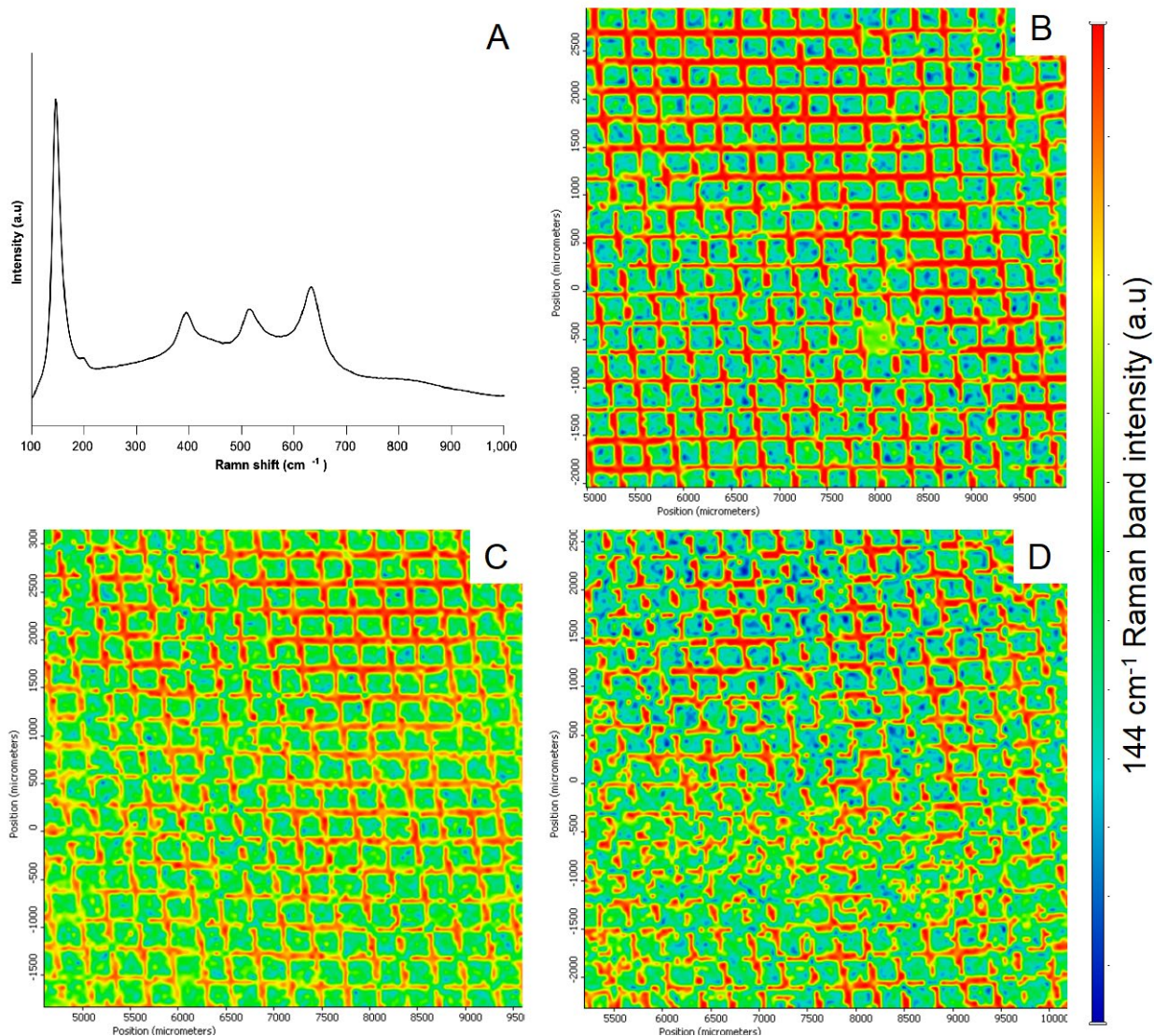
373 3.4.Durability and reusability assessment

374 The best set of conditions (sample No. 16), predicted by the model and verified
 375 experimentally, was used to assess the reusability potential of the TiO₂-coated stainless-steel
 376 mesh. As displayed in Fig. 7, no apparent reduction in photocatalytic activity was observed
 377 after 10 consecutive cycles or 360 h of testing. In Fig. 8, the Raman mapping confirmed this
 378 trend, with no obvious change in the coating's integrity being observed between the first
 379 analysis and after 180 and 360 h of testing. The visual differences observed in Fig. 8(D) are
 380 due to the bending of the sample in certain areas (mainly lower left) after multiple handlings,
 381 while performing repeated analysis. This bending of the mesh resulted in out of focus
 382 analysis, which is why some threads appear bare whilst other apertures appear coated.



383

384 *Figure 7. Reusability assessment of the TiO₂-coated mesh; MB removal percentage after 5h*
385 *for 10 consecutive cycles.*



386

387 *Figure 8. Raman maps with integrated intensities of (A) the main anatase peak at 144 cm⁻¹*

388 *of the same area after the (B) 1st, (C) 5th and (D) 10th MB degradation cycle.*

389 **4. Discussion**

390 The influence of five parameters was investigated for their role in the removal of methylene

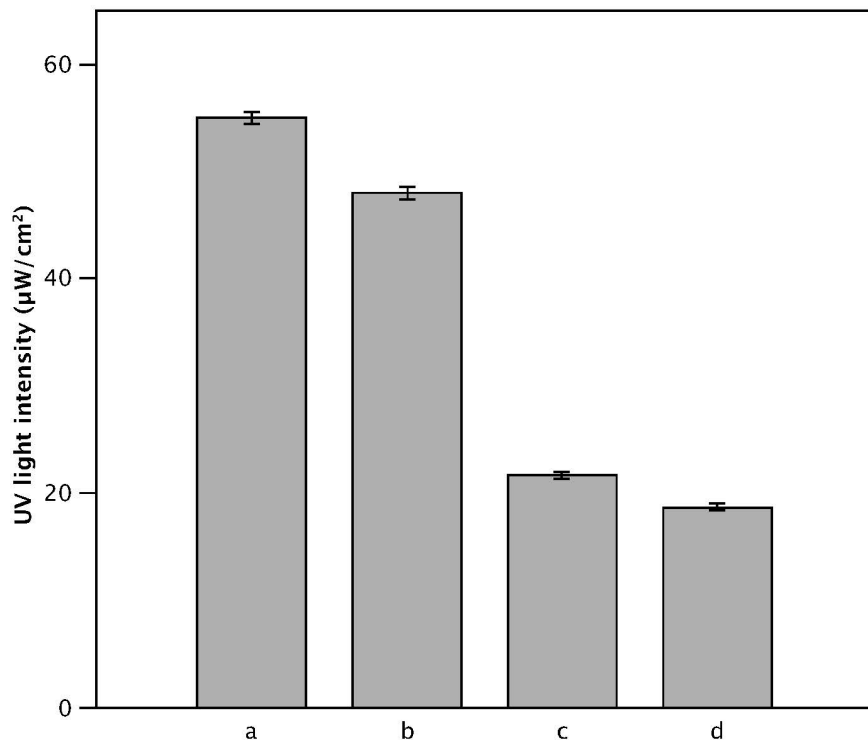
391 blue after 5 h, in this bespoke photocatalytic reactor. Using a linear regression model, UV

392 light intensity (X_1), number of TiO₂-coated mesh layers (X_2), coating thickness (X_3) and

393 initial dye concentration (X_5) were identified as the most important and influential

394 parameters. Flowrate (X_4) had no effect on the MB removal rate, at the minimum (5.14 L
395 min^{-1}) and maximum (9.54 L min^{-1}) operating conditions of the 12 V pump. This is consistent
396 with the findings of de Lasa et.al, who concluded that mass transfer was not limiting the
397 removal of MB in their photocatalytic reactor, for flowrates equal or higher than 1.7 L. min^{-1}
398 (Lasa et al., 2005). Decreasing the initial dye concentration (X_5) resulted in an increased MB
399 removal rate, which could be the result of a lower consumption of radical species by
400 intermediary products (Ahmed et al., 2011; Ajmal et al., 2014). Increasing the UV light
401 intensity (X_1) improved the MB removal, as it is known to increase the photogeneration of
402 excitons and of radical species (Ajmal et al., 2014; Cassano and Alfano, 2000; Chen et al.,
403 2007). Increasing the coating thickness (X_3) and the number of TiO_2 -coated mesh layers (X_2)
404 also improved the MB removal rate. The former has been reported as having a positive effect
405 on photocatalytic activity, with significant improvements occurring between 100 and 500
406 nm, and to a lesser extent between 500 nm and 2 μm (Daviðsdóttir et al., 2014). Increasing
407 the latter comes down to increasing the catalyst load, which is known to improve the reaction
408 rate (Yunus et al., 2017). Interestingly, a significant negative interaction between the coating
409 thickness (X_3) and the number of TiO_2 -coated mesh layers (X_2) seemed to play a role in the
410 MB removal efficiency. Overlapping two sets of mesh coated with TiO_2 for 2 h could hinder
411 light permeability, in turn decreasing the efficiency of the system. It was confirmed
412 experimentally, by measuring the UV light intensity (at 365 nm) received by a UVP UVX
413 Radiometer detector, after passing through the reactor loaded with different mesh
414 configurations (Fig. 9). Decreases of 12.7 and 13.8 % were observed, respectively, for one
415 and two sets of coated stainless-steel mesh, when the coating thickness increased from 1.1 to

416 1.6 μm . These values are only indicative, as the measurements were performed without the
 417 reflective surfaces.



418

419 *Figure 9. UV light intensity measured for different mesh configurations; (a) 1 set of mesh, 1*
 420 *h deposition; (b) 1 set of mesh, 2 h deposition; (c) 2 sets of mesh, 1 h deposition; (d) 2 sets*
 421 *of mesh, 2 h deposition.*

422

423 *Table 6. Summary of reactor characteristics*

Parameters	Unit	LCPR-I
Catalyst	-	TiO ₂
Optical bandgap	eV	3.2
Synthesis method	-	Pulsed DC Reactive Magnetron sputtering

Coating thickness	μm	1.6
Pollutant	-	Methylene blue
Catalyst loading	g.L^{-1}	0.34
Initial concentration	$\mu\text{mol.L}^{-1}$	1
Light power (peaked at 365 nm)	mW/cm^2	6.2
Degradation efficiency after 5 h of UV-A irradiation	%	93
Power consumption	$\text{Wh.}\mu\text{mol}^{-1}$	627
Flux of absorbed photons (φ)	$10^{-8} \text{ mol.cm}^{-2}.\text{s}^{-1}$	1.90
Reaction rate (r)	$10^{-14} \text{ mol.cm}^{-2}.\text{s}^{-1}$	8.01
Quantum yield (QY)	$10^{-6} \text{ molecule.photon}^{-1}$	4.22
*Figure of merit (FOM)	$\mu\text{mol.Wh}^{-1}.\text{h}^{-1}.\text{g}^{-1}$	1.14
*FOM classification: best (100), good (30 - 10), average (10 - 1) and below average (<1)		

424

425 The characteristics and performance metrics of this bespoke reactor are summarised in Table
426 6. The LCPR-I displayed rather average QY and FOM levels. This can be explained by the
427 composition of the reactor walls (PMMA), which absorbed >80 % of incident UV-A light,
428 as shown in supplementary materials. Despite this limited UV-A transmittance, LCPR-I still
429 managed to achieve a FOM of 1.14, achieving better performance than >40 % of the 85
430 systems reviewed by Anwer et al. (2019). It should be noted though, that as a metric, the
431 FOM parameter tends to favour powder-form photocatalysts, due to the “catalyst dosage”
432 component used in equation (15). Specific surface area is known to be positively correlated
433 with photocatalytic activity (Amano et al., 2010), which is negligible when comparing

434 powder-form photocatalysts of similar specific surface area. This is not the case for
435 immobilised photocatalysts, as photocatalytic reactions only occur on the film's exposed
436 surface, which is orders of magnitude smaller than their powder counterpart. This is
437 especially true for thin films produced by reactive magnetron sputtering, which tend to form
438 dense columnar structures (Kelly and Arnell, 2000).

439 Whilst the results of the current study are encouraging, there is still room for improvement
440 for this proof of concept. The interaction between coating thickness and the number of TiO₂-
441 coated mesh layers was identified as having a negative impact on the MB removal efficiency.
442 To increase the catalyst load whilst maintaining light permeability, different strategies can
443 be implemented, such as simultaneously irradiating the reactor from different angles and/or
444 using different mesh aperture sizes.

445 Future work will be aimed at coating the LCPR-I mesh, using reactive magnetron sputtering,
446 with a sunlight-activated photocatalyst, instead of TiO₂, and evaluating its effectiveness
447 against micro-organisms, pharmaceuticals and real-world wastewater samples. Fouling was
448 not investigated in this study due to the use of deionised water, but it will be in future work,
449 as microbial presence in wastewater would produce biofouling and affect the photoreactor's
450 performance. Using sunlight not only would reduce the upfront cost of the system by over
451 60%, but it would considerably reduce the amount of irradiation absorbed by the reactor
452 walls, resulting in more efficient water-treatment performance.

453 **5. Conclusions**

454 In this study, a bespoke photocatalytic reactor (LCPR-I) was built from low cost consumer
455 market parts and used to degrade a model pollutant, methylene blue. The reactor utilises

456 crystalline TiO₂-coated woven stainless-steel mesh photocatalyst, produced in a one-step
457 process by reactive pulsed DC magnetron sputtering. This deposition process is sustainable
458 and addresses the technical viability and economic feasibility challenges faced by
459 photocatalytic waste treatment. The methylene blue removal percentage after 5 h was
460 optimised by investigating the influence of UV light intensity, number of TiO₂-coated mesh
461 layers, coating thickness and water flowrate. All factors, with the exception of flowrate, were
462 found to have an influence on the removal process efficiency. 30 W UV-A, 2 layers of mesh
463 coated with 1.1 µm of TiO₂ and a flowrate of at least 5.14 L.min⁻¹ were found to be the
464 optimum conditions, leading to the removal of more than 90 % of the model pollutant under
465 5 h. The coated stainless-steel woven mesh has proven to be durable as the photocatalytic
466 activity of the material remained unchanged after 360 h of consecutive use. The findings of
467 this study, as well as the proposed reactor design, may be of considerable interest for those
468 involved in practical implementation of sustainable and efficient photocatalytic water
469 treatment processes.

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