

Supplementary Information

Comparison of photocatalytic membrane reactor types for the degradation of an organic molecule by TiO₂ coated PES membrane

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1. X-ray Diffraction (XRD) analysis of synthesized TiO₂ nanoparticles

Method and condition of XRD measurement: Direct XRD measurements of the TiO₂ layers on the membranes was not possible as the signals are superimposed by noise caused by the polymer structure of the membrane. Therefore, the excessive TiO₂ powder in suspension was refined after synthesis and used for XRD. The XRD patterns have been measured with a Rigaku Ultima IV X-ray diffraction spectrometer with Cu K α radiation (40 kV, 40 mA, scanning speed: 2 ° min⁻¹, step size: 0.05°.

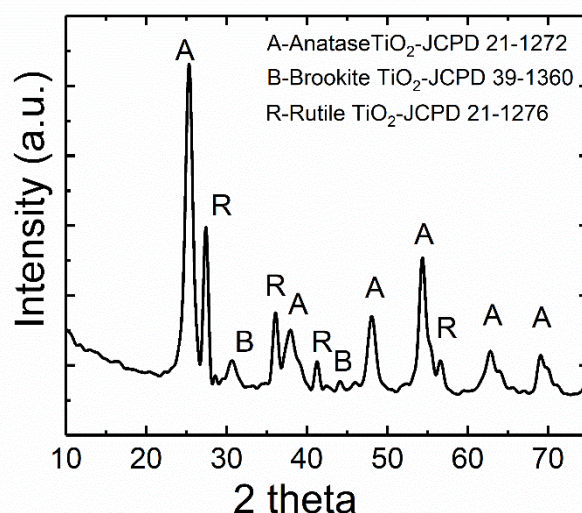


Figure SI 1 XRD spectra of the synthesized TiO₂ nanoparticles.

The XRD spectra is displayed in **Figure SI 1**. XRD spectra reveals that the mixed phase of TiO₂ (anatase, rutile and brookite) were formed that well matches with the JCPD card no as indicated in the figure [1]. The high crystallinity of the synthesized TiO₂ dispersion was confirmed by the appearance of the sharp peak in XRD spectra.

2. SEM images

To show the dispersion of the TiO₂ nanoparticles on the membrane, SEM images were taken.

Methods and conditions of measurement- For SEM imaging, the samples were sputtered with a 30 nm chromium layer with a Leybold Z400 sputter system. SEM images were taken with a Carl Zeiss Ltd. Ultra 55 SEM.

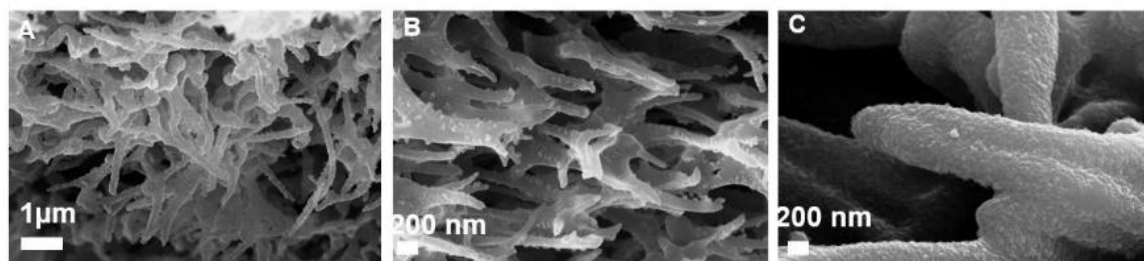


Figure SI 2 SEM images of A) top section, B) cross-section, and C) magnified portion of membrane showing the incorporated TiO₂ nanoparticles in/onto the membrane.

The SEM images (**Figure SI 2**) show that TiO₂ nanoparticles are homogeneously incorporated throughout the membrane.

3. UV-vis Diffuse Reflectance Spectra (DRS) measurement

To determine the bandgap of synthesized TiO₂ nanoparticles DRS measurement was carried out.

Methodology for Diffuse Reflectance Spectroscopy (DRS) measurement and calculation- DRS measurement has been performed in UV-vis-NIR spectrophotometer (Perkin Elmer Lambda 950, USA). Measurement has been done in % transmittance ordinate mode and the exclusion port open to exclude the specular reflection. Sample was fixed on the rear side of the integrated sphere with the incident light adjusted perpendicular to the sample and the light passing through the integrated sphere striking the center of sample on the other side of the integrated sphere. During the determination of the bandgap the diffuse reflectance value of the pristine membrane was subtracted to get the diffuse reflectance value of TiO₂ nanoparticles only.

By applying Kubelka-Munk method (which provide the conversion of reflectance data into a parameter named $F(R)$ which is proportional to the absorption coefficient (α)), the band gap was determined from the measured value of diffuse reflectance spectra using the following equations as shown in **Figure SI 3**;

$$F(R) = \frac{(1 - R)^2}{2R} \quad (S1)$$

$$(h\nu F) \cong (h\nu - E_g)^2 \quad (S2)$$

where F is the Kubelka-Munk Function, R is the reflectance, $h\nu$ is the photon energy and E_g is the band gap. By plotting $(h\nu F)^{\frac{1}{2}}$ for indirect band gap of TiO₂ against $h\nu$, the E_g can be calculated [2].

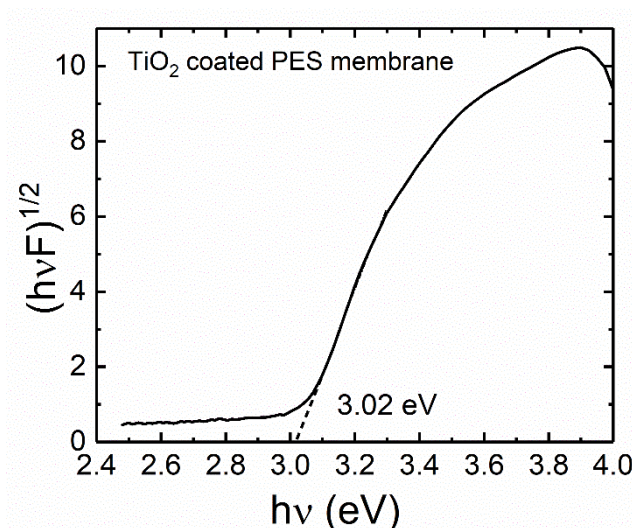


Figure SI 3 Band gap calculation from DRS spectra by Kubelka-Munk method of TiO₂ coated PES membrane sample.

The bandgap of the TiO₂ was determined to be 3.02 eV.

Although the Tauc plot obtained from Kubelka-Munk method for determining the bandgap is well established and used by several research groups, the accuracy further depends on the analyst's experience. This is attributed to the fact that the method requires manual identification of Tauc segment to be fitted. Even the different xy-aspect ratio of the Tauc plot can induce the subjectivity in recognizing the range of data considered in the straight-linear fitting, which thus read different band gap value. This systematic underestimation is even more pronounced when there are multiple or unresolved absorption edges in the Tauc plot [3, 4]. Thus, systematic analytic method should be developed.

4. Calculation of the total number of TiO₂ nanoparticles deposited on the membrane

The amount of TiO₂ nanoparticles deposited throughout the membrane coupon of size 1.3 cm diameter was calculated from TGA measurement. The average density of the anatase (density 3.89 g/cm³) [5] and rutile (density 4.3 g/cm³) phase [6] was taken considering that the deposited TiO₂ particles consist of mixed-phase as depicted by XRD analysis **Figure SI 1**. The particle size of TiO₂ was measured by SEM taking fifty nanoparticles, putting a ruler from one side of the nanoparticles to the other side of the nanoparticles, and finally taking the average.

Table S1 Parameters used to determine the number of TiO₂ nanoparticles per unit membrane area.

Parameter	Unit	Value
Diameter of membrane coupon	cm	1.3
Total weight of TiO ₂	g	1.3×10 ⁻⁰³
Density of TiO ₂	g/cm ³	4.01
Total volume of TiO ₂ per coupon (considering weight and density)	cm ³	3.24×10 ⁻⁰³
Average particles size of TiO ₂ (measured from SEM images)	cm	2.70×10 ⁻⁰⁵
Radius of each TiO ₂ particles (assuming that the particles are spherical)	cm	1.35×10 ⁻⁰⁵
Volume of each TiO ₂ particles	cm ³	1.03×10 ⁻¹⁴
Number of TiO ₂ particles per membrane coupon	-	3.15×10 ¹⁰

The total number of TiO₂ nanoparticles deposited per unit cm² of membrane area was estimated to be 2.36×10¹⁰. Thus, the total number of TiO₂ particles dispersed in the membrane used in the

continuous flow process with a 2 cm² area is 4.72×10^{10} , and the batch process with 4.1 cm² area is 9.68×10^{10} .

5. Reynolds number calculation

To explain the flow (laminar or turbulent), the Reynolds number for flow-along process is calculated using the following adapted relation [7];

$$Re = \frac{D_h \cdot u}{v_k} \quad (S3)$$

where v_k is the kinematic viscosity of the water at 22°C and it is 9.55×10^{-7} m²/s [8], D_h is the hydraulic diameter (m) of the rectangular channel of the membrane flow cell (0.0013 m), and u is the feed flow velocity (m/s), calculated by;

$$u = \frac{Q_f}{S_{cross-section}} \quad (S4)$$

where, Q_f is feed flow rate (1mL/min) equal to 1.67×10^{-8} m³/s, $S_{cross-section}$ is the cross-section area of the membrane flow cell (7×10^{-6} m²) in the flow-along process, and

6. Photolysis, adsorption and degradation profile

The possible phenomena that may decrease the initial MB concentration are: 1) Photolysis - UV light can directly decompose the MB molecules. To evaluate the contribution of photolysis, in the batch reactor, MB solution was exposed to UV light in the absence of membrane matrix and absorbance was measured at a certain time interval. In the flow-through reactor, an experiment was performed using a pristine membrane, with the total feed solution of 350 mL (running 100 mL in the dark phase and 250 mL in light phase). 2) Adsorption - MB can adsorb on either the nanoparticles or membranes. For this purpose, a filtration experiment was carried out using a TiO₂ coated membrane in the dark following a similar protocol as described above.

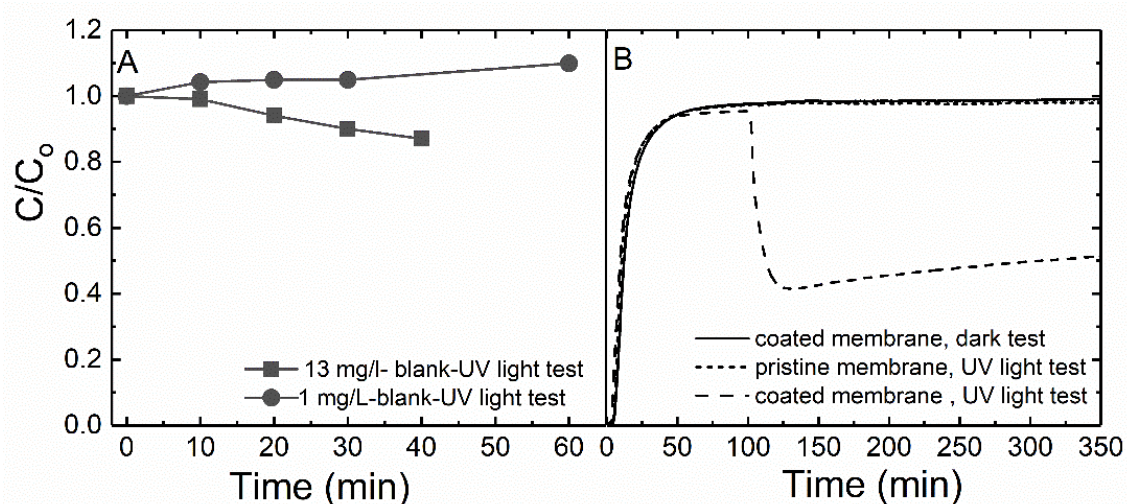


Figure S14 A) Photolysis experiment in the batch reactor using UV light with different MB concentration, B) Adsorption, and degradation profile of pristine and TiO₂ coated membrane in the flow-through reactor, (1 mg/L, 1mL/min, 10 mW/cm²).

Photolysis experiment with MB concentration 1 mg/L in the batch process shows no decrease in concentration and only a slight increase in MB concentration over the length of the experiment is observed which could be due to the evaporation of water. A slight decrease ($12 \pm 2\%$) in MB concentration is observed for 13 mg/L experiment in the batch system. In the flow-through process, the pristine membrane shows no degradation even at the presence of light.

7. Quantification of the amount of MB adsorbed in flow-through process

To quantify the mass of MB adsorbed on the membrane, an experiment was carried out in the dark phase. The UV-vis absorbance was recorded every 10 seconds and the concentration of MB was calculated accordingly until a complete breakthrough was reached (i.e. $c_p/c_f = 1$). Then, the mass balance was applied to calculate adsorbed mass as described in equation S5 [9];

$$M_{ads} = \frac{(c_f \cdot V_f - c_p \cdot V_p)}{A_{membrane}} \quad (S5)$$

where, M_{ads} is the amount of MB adsorbed per unit membrane area (mg/cm^2), $A_{membrane}$ effective membrane surface area (2 cm^2), $c_p V_p$ is the mass of permeate obtained in the dark phase, which is equivalent to the area underneath the c_p/c_f curve, $c_f V_f$ is the mass of feed that passes through the membrane, which is equal to the area of the rectangle underneath the (EC_p/EC_f) curve obtained with normalized conductivity (only background solution). EC_p is the permeate conductivity and EC_f is the feed conductivity. Using the permeate concentration calculated using the data from UV-vis, the adsorbed mass of MB can be obtained by integrating the area above the curve of c_p/c_f vs permeate volume as shown in **Figure SI 5**.

$$M_{ads} = \frac{1}{A_{membrane}} \cdot c_f \int_0^{V_f} (1 - \frac{c_p}{c_f}) dv \quad (S6)$$

However, to consider the system dispersion volume, the response of a tracer (here solution conductivity) was used to enable a more accurate mass adsorbed calculation. System dispersion volume was calculated as the area above the normalized conductivity curve (EC_p/EC_f) and therefore, equation S6 was rewritten as equation S7 and the actual mass adsorbed was obtained from the integration of area between normalized conductivity curve (EC_p/EC_f) and c/c_0 curve,

$$M_{ads} = \frac{1}{A_{membrane}} \cdot c_f \int_0^{V_f} (\frac{EC_p}{EC_f} - \frac{c_p}{c_f}) dv \quad (S7)$$

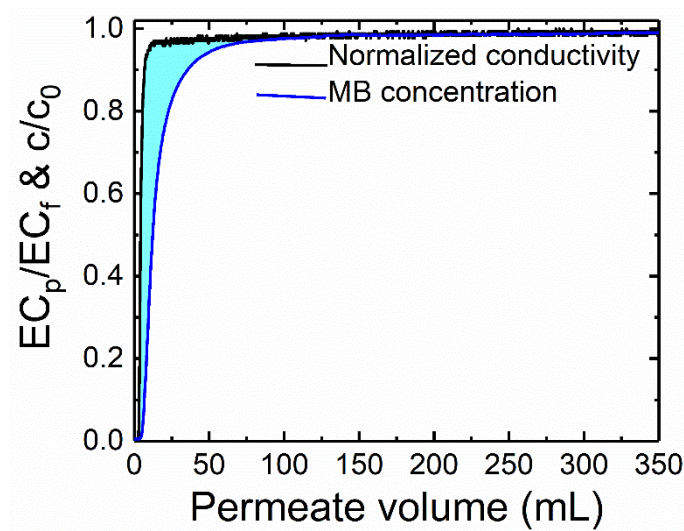


Figure SI 5 Concentration profile of normalized conductivity and MB solution in dark as a function of permeate volume.

Table S 2 Parameters used to calculate the mass adsorbed by the membrane matrix in flow-through process.

Parameters	Unit	Value
Area below the normalized conductivity curve ($C_f V_f$)	mL	340
Area below the MB curve ($C_p V_p$)	mL	329
Area between the conductivity curve and MB curve	mL	11
MB concentration	mg/L	1

Total feed volume	mL	350
Total mass in the feed	mg	0.35
Active membrane area	cm ²	2
Total mass adsorbed	mg	0.001
Total mass adsorbed per unit membrane area	mg/cm ²	0.005
% adsorbed mass	%	2.8

The loss due to adsorption was small, typically less than 3%.

8. MB concentration profile at different light intensities

Concentration profile of MB degradation at length of time when irradiated to different light intensities are displayed below.

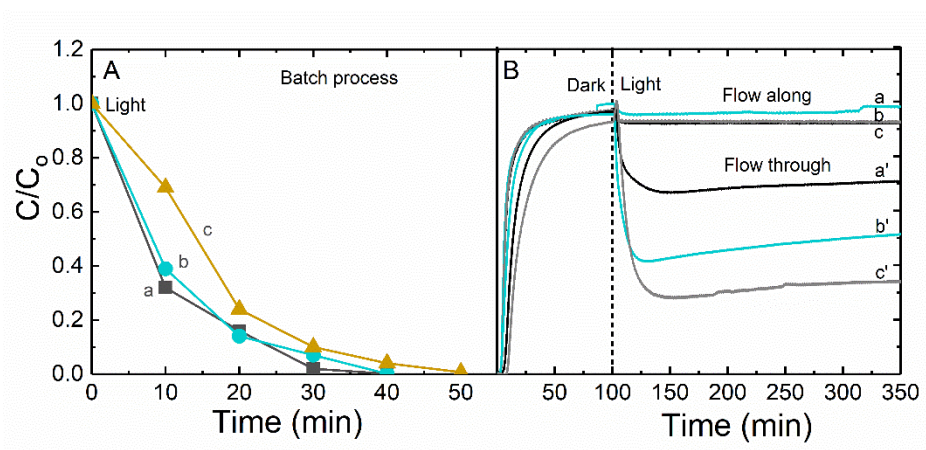


Figure SI 6 A) Concentration profile of MB operated at different light sources in batch process, (a) 13 mg/L-UV lamp, (b) 1 mg/L-UV lamp, and (c) 1 mg/L-UV LED; B) Concentration profile of MB at different light intensities at different continuous flow mode, (a and a') 2 mW/cm², (b and b') 10 mW/cm², and (c and c') 17 mW/cm² respectively; 1 mL/min flow rate, 1mg/L MB concentration.

In the batch process, complete removal (below detection limit) is achieved in 40 min (MB with 13 mg/L and 1 mg/L using UV lamp). With LED, it even takes a longer time (50 min) for complete removal of MB (1mg/L). MB removal increases with an increase in light intensity in both flow-through and flow-along process.

9. MB concentration profile at different flow rates

Concentration profile of MB removal observed at length of permeate volume when the experiment is performed at different flow rate.

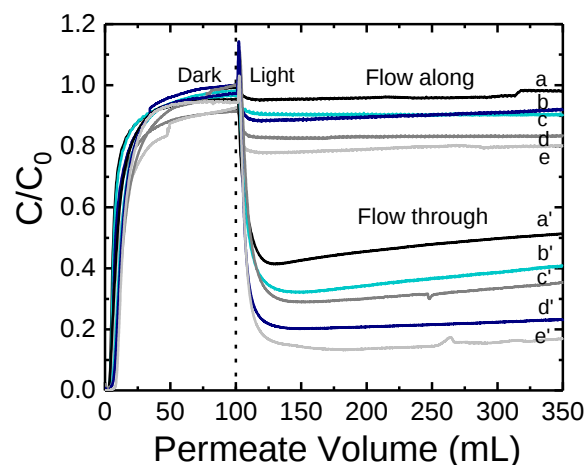


Figure SI 7 Concentration profile of MB at different flow rate at different flow mode; (a and a') 1 mL/min, (b and b') 0.7 mL/min,; (c and c') 0.5 mL/min, (d and d') 0.3 mL/min, (e and e') 0.2 mL/min respectively, 10 mW/cm² light intensity, 1 mg/L MB concentration.

MB removal increases with decreasing the flow rate in both flow-through and flow-along modes. MB removal in flow-through is higher than that of flow-along mode.

10. Calculation of the molecular diffusion

The obtained value of the residence time of MB molecules inside the pores (2×10^{-2} min) for flow-through at the rate of 1 mL/min was compared with the diffusion time of the MB and hydroxyl radical (assumed that the produced radical is hydroxyl). In case of continuous flow, this is driven by molecular diffusion and was calculated as a radial diffusion time using the following adapted relation [10];

$$t_d = \left(\frac{d_p/2}{D} \right)^2 \quad (\text{S8})$$

where d_p is the average pore diameter (2.2×10^{-7} m) (provided by manufacturer as 220 nm) and D is the diffusion coefficient of hydroxyl radical (1.63×10^{-7} m²/min) [11] and MB (0.46×10^{-7} m²/min) [12] in water.

11. Pure water flux measurement

The permeability is an important aspect to explain the throughput in flow-through process. Thus, the membrane permeability is determined by measuring the pure water flux as a function of transmembrane pressure in the flow-through process before and after the degradation experiment, where the slope is the permeability.

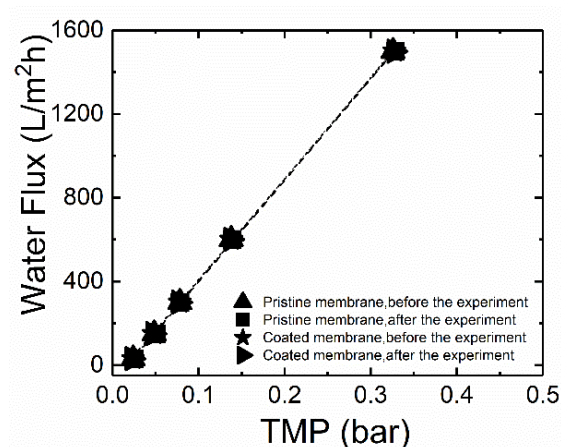


Figure SI 8 Pure water flux for pristine and TiO₂ coated membrane before and after the degradation experiment in flow-through mode; (conditions of the photocatalytic experiment, 1mL/min and; 10mW/cm²).

Permeability of both the membranes (pristine and TiO₂ coated) before and after the photocatalytic degradation experiment are: pristine (4866 and 4845 L/(m² h bar)) and TiO₂ coated membrane (4837 and 4823 L/(m² h bar)).

12. Light power calculation

The electric light power of the lamp used in the batch experiments was found on the Technical Data provided by the supplier (MagicSun®, OH M 21/25 Tanning tube), being 25 W. The electric light power of the 6 LEDs system used on the batch experiments was measured to be 5 W. The electric light power of the LED used on the flow-through and the flow-along experiment was determined as follows, using the LED performance plot **Figure SI 9** [13].

$$P = V \cdot I \quad (S9)$$

where P is the electric power (W), V is the voltage difference (Volts) and I is the electric current (Amps).

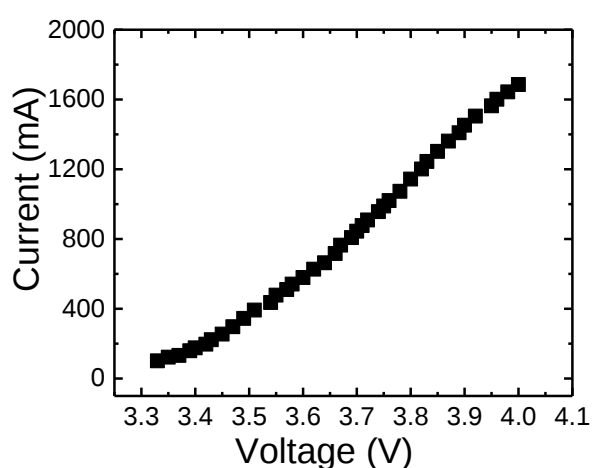


Figure SI 9 Current vs Voltage of the THORlabs M365LP1 mounted LED.

The light power applied during the experiment was 3.3 W ($P = 890 \text{ mA} \cdot 3.71 \text{ V}$).

13. Dimensions of the reactors used in the experiments

The schematic of the reactors system showing the dimension of the cell, window, channel and well, are shown below;

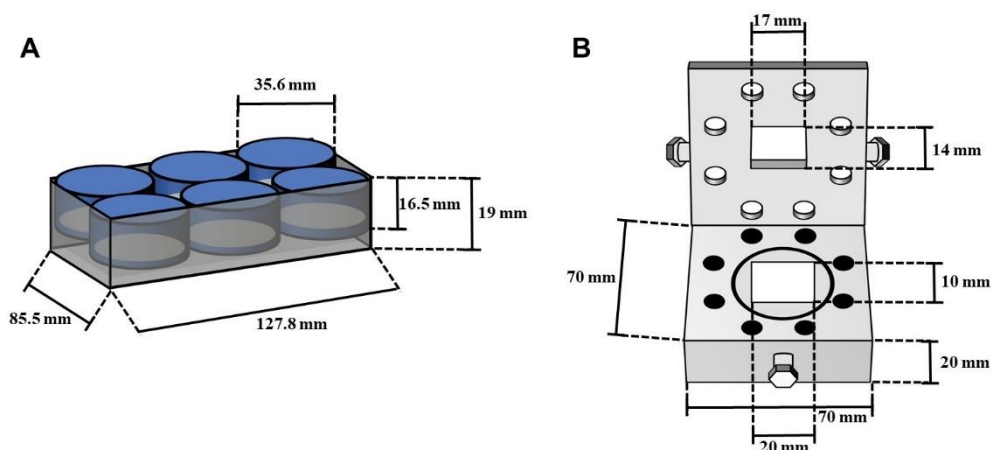


Figure SI 10 Dimensions of the A) batch, and B) flow-along/through reactors.

14. Unit conversion.

The following unit conversion factors are applied elsewhere in the manuscript.

Table S 3 Unit conversion used throughout the manuscript.

Parameter	Unit	Value
MB concentration - c	mg/L	1
	g/cm ³	1×10 ⁶
Flow-rate - Q	mL/min	1
	L/min	0.001
	L/h	0.06
	cm ³ /s	1.7×10 ⁻⁰²
Degradation rate – r'_{MB}	mol/min	1
	g/s	5.33

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