Supporting information for

Sunlight-transmitting photocatalytic membrane for reduced maintenance water treatment

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## **Text S1.** Chemicals used in the experiments

Para-chlorobenzoic acid (*p*CBA) was obtained from Sigma Aldrich, St. Louis, MO, USA. Methanol (HPLC grade) was purchased from Fisher Chemicals. Phosphoric acid (85% w/w) was supplied by EMD Chemicals, USA. Sodium sulphate (Na2SO4) was purchased from Sigma Aldrich, St. Louis, MO, USA. Sodium hydrogen phosphate (Na2HPO4·2H2O) and sodium dihydrogen phosphate (NaH2PO4·2H2O) were purchased from EMD Chemicals, USA. Sintered glass membranes coated with Degussa P25 TiO2 were prepared by a previously described method 1.

## **Text S2.** Filtration setup

Accessories in the filtration system included a TPI 665L digital manometer (Accutherm, Melbourne, Australia) to measure the transmembrane pressure (TMP) in real time, a QG20 positive displacement pump (Fluid Monitoring Inc., Syosset, USA) to drive the feed and an electronic balance (FX-3000i WP, A&D Company Ltd., Seoul, South Korea) with associated software to measure the amount of permeate. Filtration was conducted in a previously described setup 2 with manual backwashing. The modified system is presented as a schematic in Figure S1. Backwashing was carried out every hour with 15 mL of the permeate using a 40 mL syringe. The filtration mode was dead-end at a constant flux of 300 L/m2/h. Samples were collected from the backwash, permeate and feed for analysis. A 1000 W Oriel Sol 1A solar simulator equipped with a xenon arc lamp and an air mass filter to block UVC radiation provided solar radiation to the photocatalytic membrane. The spectral irradiance of the solar simulator was measured with a Maya 2000 PRO radiometer from Ocean Insight. The temperature below the solar simulator was measured using a Fisherbrand digital thermometer.



Figure S1. Schematic representation of the filtration system. The insert shows a picture of the filtration module under the solar simulator, with light travelling to the TiO2 coating through the sintered glass substrate.

**Text S3.** Pump power demand

The pump instantaneous power requirement, *Pt* (kW), at a given experiment time, *t* (h), is given by:

 (S1)

Where *qt* (L/h) is the feed flow through the membrane *pt* is the TMP (kPa), and *η* (-) is the pump efficiency assumed as 60%.

The specific electrical energy consumption of the pump, *E* (kWh/m3), is then obtained by integrating the instantaneous power over the entire experiment duration, then dividing by the total permeated volume, *Vtot* (m3), over the same time according to:

 (S2)

## **Text S4.** Quantification of hydroxyl radicals

A 0.6 mg/L solution of *p*CBA in deionised (DI) water was filtered through the membrane in dead end mode at a fixed flux of 300 L/m2/h. Permeate was collected at fixed time intervals. The concentration of *p*CBA in the collected permeate, as well as the feed, was determined by analysis with an Agilent Technology 1220 Infinity HPLC equipped with a C18 column and variable wavelength detector set at 234 nm. The mobile phase was made of 55% methanol and 45% 10 mM phosphoric acid, and the flow rate was set at 1 mL/minute. The injection volume was 30 µL. Using this method, which has been previously described 3, the *p*CBA retention time was 7.4 minutes.

The presence of photo-generated hydroxyl radicals leads to oxidation of *p*CBA, hence the steady state concentration of hydroxyl radicals ([HO•]ss ) can be calculated from Equation S3 4.

 (S3)

where *k*OH*p*CBA is the pseudo first order rate constant for the degradation of *p*CBA with hydroxyl radicals at ambient conditions, equal to 5 × 109 M−1 s−1 5.

**Text S5.** Size exclusion chromatography method

In size exclusion chromatography method, the mobile phase was a 5 mM phosphate buffer of pH 6.8 made from Na2HPO4·2H2O and NaH2PO4·2H2O. The ionic strength of the mobile phase was adjusted with Na2SO4 to give a conductivity of 6 mS to supress charge interaction with the column. The ionic strength of the injected samples was also adjusted to the same conductivity value with the prepared mobile phase. The sample injection volume was 2 mL and the flow rate was 1mL/min.

Because the sample water used for this study was that of Boulder Creek (a freshwater creek/ river), humic substances are likely to contribute to the composition of NOM present in the samples. Therefore, the SEC-fluorescence detector was set to ex: 350nm, em: 450nm, to monitor the impacts of the different membrane conditions to humic substances. Because fluorescence and absorbance detectors are limited to the detection of chromophoric DOM (that which absorbs light, associated with moieties containing pi bonding orbitals, i.e., aromatic functional groups), they do not capture the entire distribution of organic carbon. Online TOC detection allows for the measurement of all organic carbon molecules, including those that are invisible to absorbance and fluorescence detectors (i.e., aliphatic moieties and compounds). Therefore, combining TOC, absorbance, and fluorescence detection results in a more complete understanding of the nature of DOM sample composition 6, 7.

**Text S6.** Apparent molecular weight calibration method

To convert SEC elution time to apparent molecular weight (AMW), a calibration curve was generated by analysing a set of calibration standards of known molecular weights. It should be noted that because SEC separation is truly a function of hydrodynamic size (rather than the molecular weight alone), different standard compound classes yield a calibration curve specific to a given standard compound class. Therefore, conversion should be interpreted as apparent molecular weight, rather than absolute molecular weight 8. For this study, the AMW calibration curve was generated using Polyethylene glycol (PEG) standards of 106, 194, 410, 610, 1020, 1450, 3680, 8610, 16100, and 21160.

**Text S7.** Fouling indices

The hydraulic cleaning efficiency (HCE) gives a measure of the fouling that is reversed by the hydraulic backwashing process, as calculated using Equation S4 9.

= (S4)

where is the initial TMP of cycle *n* and is its corresponding final TMP.

The hydraulically irreversible fouling index (HIFI), calculated using Equation S5 when the fouling is carried out at constant flux, is a measure of fouling that is not reversed by either hydraulic backwashing or the photocatalytic processes taking place on the membrane surface 1, 9.

 (S5)

where *P0* (kPa) is the TMP of the fresh membrane and *Vs* (L/m2) is volume of permeate per unit membrane area at the time the final TMP of a cycle is measured. The HIFI is then obtained from the linear plot of *Vs* against 1/(*P0*/*Pini*).

## **Text S8.** Carbon mass balance equations

The mass of carbon (MF) in a given volume of feed, (VF), is given by Equation S6. VF is the volume of feed that leaves the feed container (used for filtration) in a given period of time.

 (S6)

where *CF* is the concentration of carbon in the feed. The mass of carbon in the dead volume of the filtration system (MD), is calculated using Equation S7.

 (S7)

where VP is the volume of collected permeate. The mass of carbon in the collected permeate (MP), is given by:

 (S8)

where *CP* is the concentration of carbon in the permeate. A portion of permeate, (with volume *VBS*), was used for backwashing the membrane, and the mass of carbon in this backwash solution coming from the permeate (MBS), was calculated by:

 (S9)

Assuming that all the carbon in the permeate portion used for backwashing (of volume VBS) all goes to the collected backwash fraction after backwashing, and all carbon removed from the membrane surface is redissolved and measured in solution, the mass of carbon in the collected backwash fraction (MBF) is given by:

 (S10)

where *CBF* is concentration of re-dissolved carbon in the collected backwash fraction. *CBF* can be measured directly from the collected backwash fraction and can be used to calculate the amount of carbon coming from permeate (volume VBS) plus that washing off the membrane from previously retained carbon (of mass MBF). In this case the volume of permeate used for backwashing (VBS) is equal to the volume of collected backwash fraction (VBF).

Assuming that all the carbon from the feed arriving at the module is sent to the membrane, the total mass of carbon retained on the membrane (MRT), is given by

 (S11)

The carbon is retained either as reversible fouling which is washed off the membrane and collected in the backwash fraction, or as irreversible fouling which remains on the membrane surface or in the pores after backwashing. However, due to the analysis method, only the re-dissolved portion of reversible fouling carbon is measured. Some reversible carbon fouling could have ended up as suspended particles, which were removed by a 0.45 um filter just before TOC analysis. The mass of redissolved carbon retained on the membrane as reversible fouling (MRR) is given by:

 (S12)

The mass of carbon retained on the membrane as irreversible fouling, as well as that which did not go back into solution, referred to as lost carbon (MIL) can then be determined by:

 (S13)

The contribution to total retained carbon (MRT) of the redissolved reversible carbon (MRR) and lost carbon (MIL) can be presented as a normalised proportion of MRT in units of mg C/mg CF, standing for mg of carbon per mg of carbon fed to the membrane.

 (S14)

where *M* is either *MRT* or *MIL*.

For an amount of carbon arriving at the membrane surface, the percentage removal is given by

 (S15)

## **Text S9.** Contact time

The contact time, *tc* (s) of DOM with the photocatalytic TiO2 layer of thickness 15 µm 1 was calculated using Equation S16 10:

 (S16)

where *δ* is the thickness of the membrane (µm) and *φ* represent is the porosity (0.44 2), and *J* is the membrane flux (L/m2/h).

## **Text S10.** Rejection % based on HPSEC

For each detection method, the total signal for each particular sample was obtained by integrating each curve. The obtained areas where then used to calculate the membrane rejection by:

 (S17)

where *Aperm* and *Afeed* are the areas for the permeate and feed signals, respectively.

|  |  |
| --- | --- |
| **(a)** | **(b)** |
| **(c)** |  |

Figure S2. The rejection of AMW fractions and total rejection based on TOC (a), fluorescence (b) and UV254 (c)

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