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HAL Authorization

1 **Title: Photocatalysis for MBR Effluent Post-Treatment: Assessing the Effects of Effluent**
2 **Organic Matter Characteristics**

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17
18 **Abstract:** Dissolved organic matter (DOM) poses a serious challenge to applied photocatalysis.
19 Membranes may offer a promising synergistic opportunity to enable efficient photocatalysts in the
20 presence of DOM. Membrane bioreactor (MBR) effluent from a municipal treatment plant was studied
21 to elucidate the effects of filtration and organic matter composition on photocatalysis. Effluent
22 samples were collected from MBR units during routine operation and before/after chemical cleaning.
23 Additional DOM samples from the bulk supernatant were separated into colloidal, hydrophobic and
24 transphilic fractions, providing a novel examination of the inhibition potential of DOM. These DOM
25 fractions and the effluent organic matter (EfOM) samples were then characterized utilizing three-
26 dimensional excitation–emission matrix (3DEEM) fluorescence spectroscopy and assayed for their
27 potential to inhibit TiO₂-mediated photocatalytic degradation of a probe compound, *para*-
28 chlorobenzoic acid (*p*CBA). The colloidal fraction of DOM was found to exert the strongest

29 inhibition, followed by the transphilic, then the hydrophobic fractions; at 5 mgC/L, these fractions
30 reduced the photodegradation rates by approximately 75%, 27%, and 17%, respectively. Of the
31 effluent samples, EfOM from the recently-cleaned membrane caused the greatest inhibition of
32 photocatalysis (~100% reduction at 0.5 to 2.0 mgC/L), whereas the effluent from the fouled membrane
33 provided the least inhibition (~33% reduction at 2.0 mgC/L). The 3DEEM analysis predicted
34 inhibitory action of both DOM and EfOM, based on total fluorescence volumes. Results here
35 demonstrate the prospective utility of combining membrane technologies with photocatalytic
36 processes.

37

38 **1. Introduction**

39 As the human population continues to grow, careful utilization of natural resources becomes
40 increasingly more important. Water usage, and particularly reuse, is a critical topic for many
41 communities.^{1,2} The development of membrane bioreactor (MBR) technology has been an important
42 step towards wastewater reuse, given substantial advantages over conventional activated sludge
43 systems in terms of improved efficiency and effluent quality.³ Despite these benefits that stem from
44 the use a physical barrier (membranes), several types of contaminants can pass through the membranes
45 and pose significant health risks upon release of the effluent into the environment. Indeed, viruses
46 have been found in the effluents of state-of-the-art MBR treatment plants.^{4, 5} In addition,
47 pharmaceuticals^{6, 7} and, more recently, antibiotic resistant genes have drawn attention as significant
48 concerns posing environmental and health risks.⁸ Thus, MBR systems require a disinfection step post-
49 filtration to provide a safeguard. Although UV disinfection can be used in lieu of chlorination, and
50 thereby avoid the necessity for an added dechlorination step, there are disadvantages: UV treatment
51 does not significantly degrade antibiotic resistant genes⁸ and many pollutants are recalcitrant to UV at
52 commonly applied UV doses.⁹

53 Given these post-filtration challenges, an integration of innovative technologies could provide the key
54 functionality to eliminate the remaining hazards from MBR effluent. In particular, photocatalytic
55 materials applied in conjunction with existing UV dosing systems could produce reactive oxygen to

56 destroy these contaminants via advanced oxidation processes.⁹⁻¹² Germicidal UV radiation, a subset of
57 the spectrum of short-wavelength UV light, often called UVC,^{13, 14} can be enhanced by the addition of
58 photocatalytic processes to promote the production of reactive oxygen species (ROS). These ROS are
59 known to be particularly effective at inactivating viruses compared to bacteria which have protective
60 cell membranes.¹⁵⁻¹⁸ For example, the inactivation kinetics *Escherichia coli* by hydroxyl radicals
61 ($\cdot\text{OH}$) or by singlet oxygen ($^1\text{O}_2$) have been shown to have a lag-phase where the cell membrane
62 protects the bacteria's intracellular components against ROS attack,^{15, 16, 18} whereas the genetic and
63 essential components of viruses, such as MS2 bacteriophage, have very little protection and therefore
64 no delay in their inactivation kinetics.^{15, 16} A combined UVC-photocatalytic system is a plausible
65 conception that could serve as an advanced oxidation process to oxidize pharmaceutical compounds in
66 addition to providing disinfection activity.¹⁰

67 Application of photocatalytic processes to natural or waste waters faces a significant challenge in the
68 form of non-target organic matter interferences. In the case of MBRs, effluent organic matter (EfOM)
69 contains a variety of molecules that are known to quench hydroxyl radicals ($\cdot\text{OH}$),¹⁹ which are
70 generally the most important ROS in any advanced oxidation—including TiO_2 mediated
71 photocatalysis. MBR EfOM is a complex mixture of organic molecules such as proteins,
72 polysaccharides, humic substances and nucleic acids.²⁰⁻²³ These molecules originate primarily from
73 microbial activity (soluble microbial products, SMPs), produced during secondary biological treatment
74 (via suspended or attached growth processes) , and are typically found at concentrations ranging from
75 3 to 25 mgC/L.^{21, 22, 24-27} EfOM can interfere with photocatalytic treatment through different inhibitory
76 mechanisms. First, EfOM absorbs significant amounts of UV light, limiting the amount of photons
77 available for catalyst excitation.²⁸ Second, EfOM quenches ROS, preventing reactions with the target
78 compounds or microorganisms.^{29, 30} This competition for ROS between the non-target EfOM and the
79 target constituents can occur in two ways: scavenging of surface-bound ROS by EfOM and quenching
80 of bulk phase ROS.^{15, 29, 31, 32} Within the complex mixture of EfOM, less than 2% of the dissolved and
81 colloidal organic materials are considered target contaminants, such as viruses or pharmaceuticals that
82 originate from the influent wastewater;³³ thus, most photocatalytically generated $\cdot\text{OH}$ radicals will be

83 quenched by reactions with non-target EfOM. Indeed, EfOM has been reported to scavenge between
84 65 and 95% of $\cdot\text{OH}$ in conventional effluents and is considered the most important $\cdot\text{OH}$ -scavenger in
85 such systems.^{34, 35} EfOM constituents, such as fulvic acid and humic acid (HA), have a net negative
86 charge above pH 3 due to the presence of phenolic and carboxylic groups.^{36, 37} These molecules can
87 therefore interact favorably with and adsorb onto the polar surface of TiO_2 , reacting directly with ROS
88 production sites.

89 It is important to understand the factors that control surface and bulk quenching mechanisms; ROS-
90 EfOM reactivity and EfOM-photocatalyst adsorption affinities drive bulk and surface quenching
91 routes, respectively. Different ROS have differential reactivities; for example, singlet oxygen ($^1\text{O}_2$) is
92 less reactive and more selective than $\cdot\text{OH}$.³⁸ Likewise, EfOM constituents may also vary in propensity
93 to react with ROS, with some compounds being recalcitrant to strong oxidants, while others readily
94 react with weaker ROS, such as $^1\text{O}_2$.^{30, 39} With regard to adsorption interactions, the nature of the
95 photocatalyst surface will determine the type of EfOM molecules that will adsorb onto the
96 photocatalyst surface. These types of interactions have been studied in depth for the case of membrane
97 fouling by organic matter,⁴⁰⁻⁴² and offer potential insights into DOM-photocatalyst interactions.

98 Membrane technology can be used to selectively remove fractions of organic matter. In the case of an
99 MBR treating municipal wastewater, the membrane's material, pore size, and fouling state affect its
100 selectivity and, therefore, the composition of the EfOM.⁴³ It is known that, in general, hydrophilic
101 macromolecular and colloidal portions of organic matter cause more reversible membrane fouling than
102 other fractions in MBR systems by forming a cake layer.^{41, 44, 45} Fouling changes the effective pore size
103 and surface characteristics of membranes; consequently, permeate quality changes over the operational
104 timeline, since the last chemical cleaning event.⁴⁶⁻⁴⁸ Membrane operation may control DOM retention
105 and thereby the composition of DOM that passes through (EfOM); therefore, the time since last
106 cleaning event could be an important parameter when considering the use of effluent disinfection
107 strategies. The extent to which membrane operation time can be used as a control EfOM quality is not
108 well known. A better understanding of the variability of EfOM constituents as a function of membrane
109 operational parameters is critical for applying post-filtration disinfection technologies. Elucidating the

110 effects of membrane operation on EfOM content provides an excellent opportunity to scrutinize the
111 effects of EfOM constituents on photocatalytic processes, a significant area of need for the field of
112 photocatalytic water treatment.

113 While TiO₂ systems have been studied extensively, the mechanisms driving ROS inhibition by DOM
114 are poorly understood. A recent literature review quantified the number of research articles
115 investigating “photocatalysis” and “natural organic matter” and found that of the 17,500 papers found
116 when searching for photocatalysis, only 0.8% (137) also referenced DOM.⁴⁹ The segregation of DOM
117 into fractions to discern phenomenological effects of constituents on photocatalytic processes is
118 therefore a critical step towards practical application of photocatalysts. A study completed in 2014 on
119 the effects of size-fractionation of DOM on the photocatalytic degradation of DOM by TiO₂ is perhaps
120 the first report to scrutinize the inhibitory mechanism by analyzing fractionated DOM samples.⁵⁰ The
121 approach in the present study utilizes EfOM from differentially fouled bioreactor membranes and
122 functionally fractionated bioreactor DOM to provide a novel assessment of inhibitory mechanisms of
123 DOM in TiO₂ photocatalysis.

124 Bulk supernatant DOM and EfOM samples collected in 2015 and 2016 from an operational MBR in a
125 municipal wastewater treatment plant (WWTP) are studied here. Fractionation of samples in terms of
126 DOM size and hydrophobicity, a method commonly used to isolate organics, was applied to MBR
127 bulk supernatant. Here, the effects of different fractions of bulk supernatant DOM and EfOM samples
128 on photocatalytic processes are assessed to identify the most important fractions to reject during
129 filtration. Three-dimensional fluorescence excitation-emission matrix (3DEEM) analysis is employed
130 to characterize the resultant DOM from fractionation procedures and the MBR effluent samples, to
131 better forecast and understand their effect on photocatalysis processes. 3DEEM is increasingly
132 employed to understand DOM evolution in wastewater systems.^{51, 52} A recent study also highlighted
133 that 3DEEM can be used to distinguish proteins from biopolymers and humic substances and to
134 quantify building blocks, with potential use as an on-line indicator to describe DOM fate and
135 behavior.⁵³ Further, this technique has distinguished the effects of different types of DOM on water
136 treatment technologies (i.e., membrane fouling, UV attenuation, and disinfection byproduct

137 formation).^{43, 54-56} Inhibitory profiles of the DOM fractions and EfOM samples are established by
138 measuring the photodegradation of a molecular probe as a function of total organic carbon (TOC)
139 concentration. Inhibition mechanisms are discussed in the context of an experimentally validated
140 model that accounts for surface and bulk phase quenching processes simultaneously.²⁹ Finally,
141 comments are made on the prospective utility of photocatalytic membrane reactors (PMRs)⁵⁷⁻⁵⁹ as a
142 combined treatment process.

143

144 **2. Materials and methods**

145

146 2.1. Chemicals

147 Humic acid and 4-chlorobenzoic acid were obtained from Alfa Aesar (Haverhill, MA). Titanium
148 dioxide (99.9% Anatase) was purchased from Alfa Aesar with a nominal particle size of 32 nm and
149 surface area of 45 m²/g. Ultrapure water (>18.2 MΩ-cm) was produced using a Nanopure Infinity
150 system (Thermo Fisher Scientific Inc., Waltham, MA). HPLC solvents were HPLC-grade and
151 obtained from Alfa Aesar.

152 2.2. EfOM sampling

153 EfOM samples were collected from a full-scale MBR wastewater treatment plant (La Grande Motte,
154 France), which treats municipal wastewater and serves a population of approximately 60,000. The
155 plant performs biological removal of nitrogen (nitrification and denitrification) and phosphorus. The
156 plant comprises four MBR tanks, each equipped with KUBOTA Submerged Membrane Units®
157 (SMUs, KUBOTA, Japan), which are flat sheet microporous membranes made of chlorinated
158 polyethylene with an average pore size of 0.2 μm and a nominal pore size of 0.4 μm. Only two MBR
159 tanks were studied. Here we define MBR1 as the unit which underwent chemical cleaning and MBR2
160 as a reference unit that did not undergo chemical cleaning during the sampling period. MBR2 was two
161 months into a three- to four-month cycle and therefore was chosen to represent a membrane during
162 normal operation. To assess the cleaning effect, activated sludge (AS) and permeate samples were
163 taken from MBR1 and MBR2 one day before and one day after the cleaning procedure took place for

164 MBR1 (June 2016). After sampling, AS samples were filtered with a 1.2 μm glass microfiber filters
165 (Whatman GF/C) to collect the dissolved portion of the AS, labeled as the bulk supernatant (BSN).
166 Hence, four samples from the MBR1 cleaning campaign and two samples from MBR2 were collected
167 and analyzed for this study: and each sample was given a reference name as shown in Table 1.

168 In addition to the samples taken to assess the effects of membrane cleaning, 500 L of AS were also
169 collected from MBR1 in June 2015 to perform DOM fractionation using dialysis and XAD-resins.
170 Prior to fractionation the AS was filtered successively through 50 μm and 2 μm polypropylene filters
171 to collect BSN. Next, softening was performed using a sodium cation-exchange resin (Purolite,
172 France) to remove calcium and magnesium ions, to avoid ion complexation with DOM and scaling
173 during the following step: reverse osmosis (RO).⁶⁰ DOM in the BSN sample was concentrated via RO
174 in order to minimize the time required for the fractionation step. A Filmtec TW 30 membrane was
175 used for the RO process, since it is known to be more resistant to DOM adsorption.⁶¹ The RO process
176 effectively concentrated the BSN by 100-fold which was subsequently used to perform DOM
177 fractionation.

178 2.3. DOM fractionation

179 The first fractionation step consisted of isolating the colloidal portion of DOM by size exclusion, using
180 dialysis (3.5 kDa, Spectra/Por 6 Dialysis Membrane) against HCl (0.01 mol/L, pH 2). Next, organic
181 colloids were separated from colloidal silica and precipitated salts by dialysis (3.5 kDa) against 0.2
182 mol/L HF.⁶² The dialysate, approximately 30 L of HCl solution containing DOM compounds with a
183 molecular weight smaller than 3.5 kDa, was then passed through XAD8 and XAD4 resins (Amberlite,
184 Sigma Aldrich) arranged in tandem. This step allowed for the collection of hydrophobic (HPO) and
185 transphilic (TPI) fractions.^{42, 63} The hydrophilic (HPI) fraction, composed of low molecular weight
186 hydrophilic DOM and salts, was collected in the outlet of the resins tandem. This fraction, however,
187 was not used in the study because the solution contained highly concentrated salts, which co-
188 precipitate with the organic matter. Removing these salts, while possible, would have required a
189 complex purification step called azeotropic distillation.⁶⁴ To collect HPO and TPI fractions adsorbed

190 onto XAD resins, elution with an acetonitrile/MQ water solution (75/25% v/v) was performed,
191 followed by evaporation and freeze-drying of the respective organic matter samples.

192

193 Table 1. Nomenclature of samples and fractions based on their respective MBR units, sampling
194 period, or fractionation procedure.

Label	Collection	Description
BSNf-MBR1	MBR1, Bulk Supernatant	Fouled membrane (Pre-wash)
BSNw-MBR1	MBR1, Bulk Supernatant	Washed membrane (Post-wash)
BSN-MBR2	MBR2, Bulk Supernatant	Midpoint between chemical cleaning events
Pf-MBR1	MBR1, Permeate	Fouled membrane (Pre-wash)
Pw-MBR1	MBR1, Permeate	Washed membrane (Post-wash)
P-MBR2	MBR2, Permeate	Midpoint between chemical cleaning events
C	MBR1, Bulk Supernatant	Colloidal fraction
HPO	MBR1, Bulk Supernatant	Hydrophobic fraction
TPI	MBR1, Bulk Supernatant	Transphilic fraction

195

196 2.4. DOM characterization

197 2.4.1 TOC and UV₂₅₄ absorbance measurements

198 TOC analysis was performed using a TOC-VCSH Shimadzu analyzer (Shimadzu Japan). The UV₂₅₄
199 absorbance was measured in a 1 cm quartz cuvette using a UV-VIS spectrophotometer (UV-2401PC,
200 Shimadzu, Japan). The specific UV absorbance (SUVA₂₅₄) was then calculated as the ratio of UV₂₅₄
201 absorbance and TOC value.⁶⁵ These analyses are reported in Table S1.

202 2.4.2. 3DEEM analysis

203 Fluorescence spectra were obtained using a Perkin-Elmer LS-55 spectrometer (USA) and a procedure
204 described elsewhere.⁵³ Spectra were divided into five regions as defined by Chen et al.,⁵⁴
205 corresponding to different groups of fluorophores. The regions were categorized by excitation-
206 emission ranges, as noted in Table 2. Region I is associated with aromatic protein-like fluorophores
207 type I (tyrosine type); Region II is associated to aromatic protein-like fluorophores type II (tyrosine
208 type); Region III corresponds to fulvic acid-like fluorophores; and Region IV and V are associated
209 with SMP-like fluorophores (tryptophane type) and humic acid-like fluorophores, respectively.

210 Table 2. Excitation and emission wavelength classifications of fluorophores.

	Region I	Region II	Region III	Region IV	Region V
Excitation, nm	200 – 250			250 – 350	250 – 500
Emission, nm	280 – 330	300 – 350	380 – 600	280 – 380	380 – 600

211

212 For qualitative analysis, spectra are represented in A.U. (Arbitrary Unit) and rejected fraction spectra
 213 (R) were calculated by subtracting permeate spectra from the BSN spectra, in order to better visualize
 214 the constituents that are rejected by the membrane. For semi-quantitative analysis, the volume of
 215 fluorescence $\Phi(i)$ (Raman Unit.nm²) normalized by the Raman spectra,⁶⁶ consisting of the integration
 216 of the spectral regions, was calculated in the different spectral regions using the following equation
 217 taken from the fluorescence regional integration (FRI)⁵⁴ method:

$$\Phi(i) = MF(i) \sum_{ex} \sum_{em} I(\lambda_{ex}\lambda_{em})\Delta\lambda_{ex}\Delta\lambda_{em}$$

218 (Eq. 1)

219 where MF(i) is a multiplication factor, $\Delta\lambda_{ex}$ is the excitation wavelength interval (2 nm), $\Delta\lambda_{em}$ is the
 220 emission wavelength interval (0.5 nm) and $I(\lambda_{ex}\lambda_{em})$ is the fluorescence intensity at each excitation-
 221 emission pair (Raman units). $\Phi(i)$ normalization was necessary to compare values from different
 222 regions of the 3DEEM response. To do so, MF(i) was calculated using Equation 2.

$$MF(i) = \frac{Total\ spectra\ area}{Specific\ region\ area(i)}$$

223 (Eq. 2)

224 For percentage analysis, the ratio between the volume of fluorescence of each region and the total
 225 volume was used.

226 2.5. Photochemical experiments

227 Photochemical experiments were conducted in an enclosed UV cabinet with a magnetically stirred
 228 photoreactor at room temperature. A 15 W low pressure mercury lamp (Sankyo Denki Co.,) was used
 229 as a UVC light source. The distance between the light source and reaction vessel was 20 cm. The
 230 irradiance at 254 nm at the location of the vessel was measured to be 295 $\mu\text{W}/\text{cm}^2$ with a BLUE-Wave
 231 UVNb-25 Spectrometer (StellarNet Inc., Tampa, FL). The UV/Vis emission spectrum for the lamp,
 232 shown in Figure S1, was also recorded. The DOM fractions and EfOM samples described above,

233 along with HA, were used to show the inhibitory effect of organic matter on photocatalytic
 234 degradation of target pollutants. Experiments utilized 15 ml of solution, containing 5 $\mu\text{g/L}$ TiO_2 with
 235 10 μM para-chlorobenzoic acid (*p*CBA) as a probe compound that has a known reaction rate constant
 236 with $\cdot\text{OH}$.³⁰ HA, DOM fractions, or EfOM samples in various concentrations were added to the
 237 reaction solutions to assess the quenching potential of each fraction. Sample aliquots of 0.5 mL were
 238 taken at fixed time points and analyzed for *p*CBA concentration via HPLC, according to methods
 239 reported elsewhere.⁶⁷ Briefly, this analysis was conducted with an Agilent HPLC (Agilent technology,
 240 1260 infinity) using a C18 (125 mm) column using acetonitrile and 10 mM phosphoric acid as mobile
 241 phase solvents (60:40). The flow rate was 0.5 mL/min and the detection wavelength was 234 nm. For
 242 all photochemical reactions, *p*CBA degradation rates were obtained by linear regression of plots of
 243 *p*CBA concentration versus radiant fluence ($\mu\text{J}/\text{cm}^2$). Fluence values were calculated according to
 244 Bolton and Linden (2003),⁶⁸ as described previously.⁵⁷ Importantly, these calculations account for
 245 reductions in UV_{254} transmission by using sample-specific UV_{254} absorbance values and the
 246 transmission distance inside the reactor. The resulting observed photodegradation rates (k_{obs}) were, to a
 247 good approximation, first order with respect to radiant exposure (H , $\mu\text{J}/\text{cm}^2$) such that the units of k_{obs}
 248 are reported as ($\text{cm}^2/\mu\text{J}$), according to equations (3-6):

$$249 \quad \frac{dC}{dt} = k'_{\text{obs}}C, \quad (\text{Eq. 3})$$

$$250 \quad \frac{1}{H(\mu\text{J}/\text{cm}^2)} \frac{dC}{dt} = \frac{1}{H(\mu\text{J}/\text{cm}^2)} k'_{\text{obs}}C, \quad (\text{Eq. 4})$$

$$251 \quad \frac{dC}{dH} = k_{\text{obs}}C, \quad (\text{Eq. 5})$$

252 and

$$253 \quad k_{\text{obs}} \left(\frac{\text{cm}^2}{\mu\text{J}} \right) = \frac{k'_{\text{obs}} \left(\frac{1}{\text{s}} \right)}{E \left(\frac{\mu\text{W}}{\text{cm}^2} \right)}. \quad (\text{Eq. 6})$$

254 Here, k'_{obs} (s^{-1}) is the first-order degradation rate constant of *p*CBA, C is the molar concentration of
 255 *p*CBA, and E is the irradiance ($\mu\text{W}/\text{cm}^2$) at 254 nm. The differences in the k_{obs} in the presence or
 256 absence of organic compounds were used to quantify the inhibitory effect of these compounds.
 257 Control experiments were also conducted in the absence of organic matter, TiO_2 , or light.

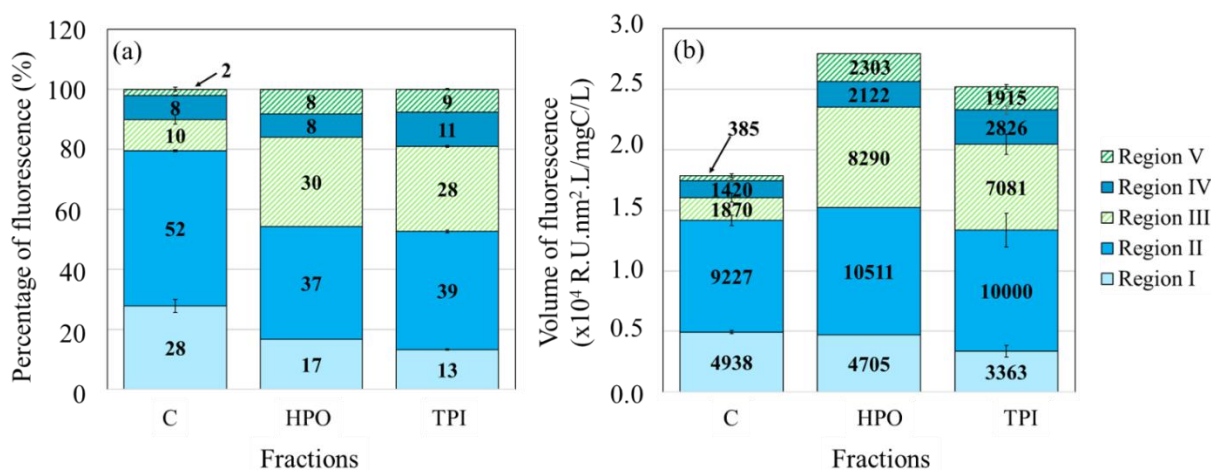
258

259 **3. Results**

260 3.1. Isolated DOM fractions

261 Prior to performing photocatalytic experiments, DOM fractions were characterized using 3DEEM to
 262 identify molecular characteristics of DOM within each fraction. The 3DEEM spectra compiled for the
 263 fractions are available elsewhere²³ and were used here to quantify the volume of fluorescence and the
 264 percentage of fluorescence of each region in Figure 1.

265



266

267 Figure 1. (a) Percentage of fluorescence and (b) Volume of fluorescence of the colloidal (C), HPO
 268 fractions prepared at 1 mgC/L. Region I, Region II, Region III, Region IV and Region V correspond to aromatic
 269 proteins-like type I, aromatic proteins-like type II, fulvic-like, SMP-like and humic-like fluorophores,
 270 respectively.

271

272 3DEEM analysis showed that each of the three DOM fractions contained both classes of fluorescent
 273 compounds: proteins (Regions I, II and IV) and humic substances (Region III and V). However, as
 274 seen in Figure 1a, DOM fractions exhibited different fluorescent properties, reflecting differences in
 275 their compositions. The percentages of fluorescence of HPO and TPI fractions were similar for all
 276 regions and had a dominant proportion of aromatic protein-like type II and fulvic-like fluorophores
 277 (Figure 1a). That HPO and TPI compositions did not vary significantly in terms of fluorophore content
 278 expected; a study on EfOM of wastewater treatment plants also found that these fractions were similar
 279 in terms of fluorophore composition.⁶⁹ For the colloidal fraction, 80% of the fluorescent compounds
 280 were aromatic protein-like type I and II fluorophores. Recent studies showed that both protein-like and
 281 humic-like fluorophores impact photocatalytic performance. Protein-like constituents were found to

282 react with $\cdot\text{OH}$ radicals in bulk solution,⁵⁵ with reported reaction rate constants of amino acids,
283 proteins, and peptides with $\cdot\text{OH}$ ranging from 1.7×10^7 to $1.05 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ (the rate constant between
284 *p*CBA and $\cdot\text{OH}$ is similar at $5.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$),⁷⁰⁻⁷² while humic-like compounds, having a large number
285 of carboxylic groups, adsorbed onto TiO_2 surfaces, particularly at low pHs.⁷³ Thus, the high proportion
286 of fluorescing compounds in Region I and II in colloids, suggests that the colloids may be more
287 reactive with $\cdot\text{OH}$ than HPO and TPI. On the contrary, HPO and TPI are expected to exhibit more
288 surface-phase quenching by adsorbing more strongly onto TiO_2 and than the colloids.

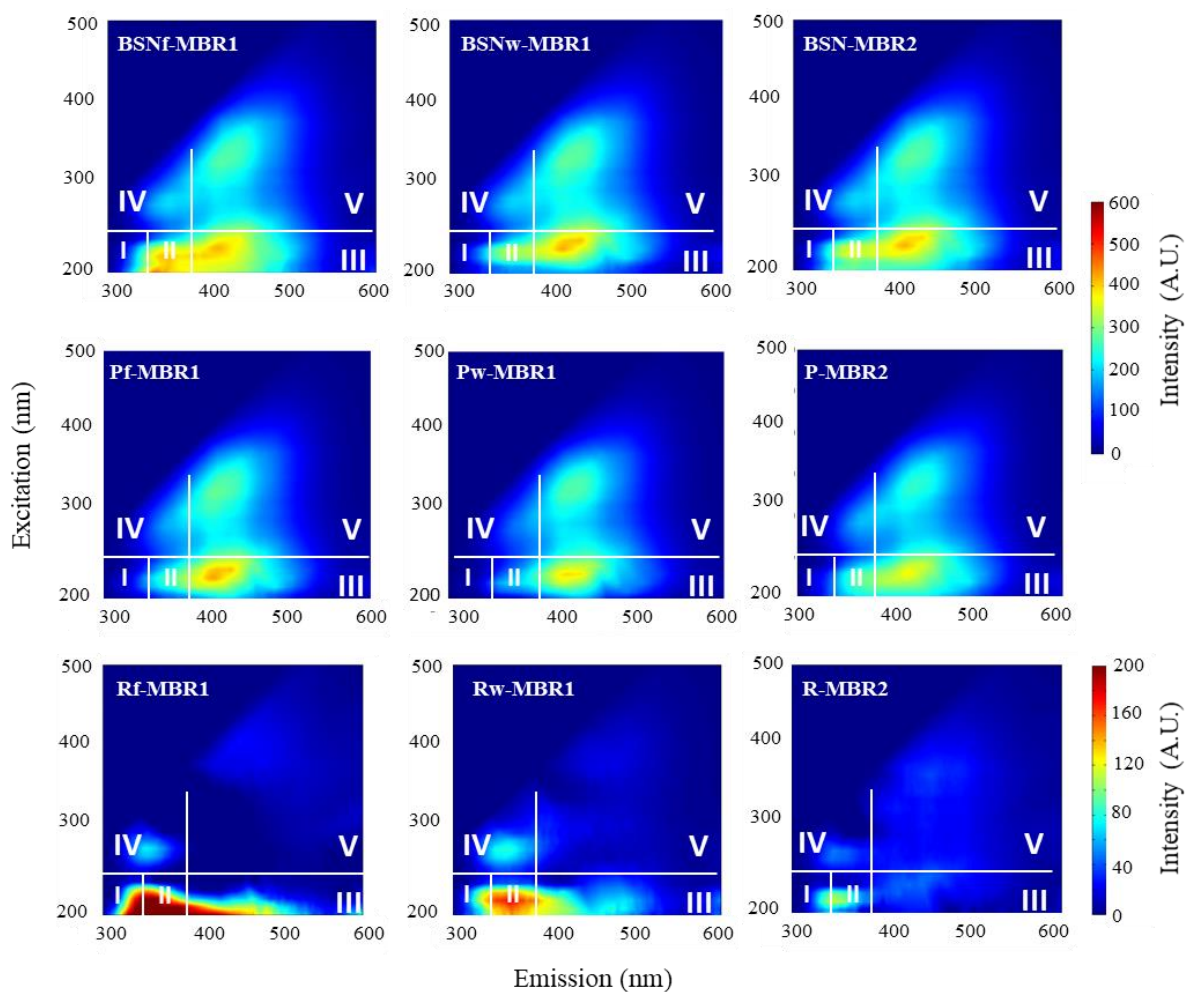
289 The volume of fluorescence is an indicator proportional to the concentration of fluorophores contained
290 in each region. The higher electron density of fluorophores compared with other moieties could yield
291 higher reactivity with ROS, and it would follow, then, that the higher the volume of fluorescence, the
292 higher the quenching of photocatalysis. Thus, from Figure 2b, and hypothesizing that surface-phase
293 quenching is the most problematic for photocatalysis, the DOM quenching potency could be expected
294 in the following order: HPO>TPI>C. A similar analysis can be conducted by measuring the SUVA_{254}
295 values as a representation of average aromatic moiety content, which is known to loosely indicate
296 DOM hydrophilicity.⁷⁴ In general, DOM compounds with higher SUVA_{254} values are considered to be
297 more hydrophobic than those with lower values.⁷⁵ In addition, higher SUVA_{254} values correspond to
298 more aromaticity, which could indicate higher reactivity with ROS, given the electron rich moieties.
299 The SUVA_{254} values for the colloidal, HPO, and TPI fractions were measured to be 1.8, 2.2, and 1.6
300 $\text{L} \cdot \text{mg}^{-1} \cdot \text{m}^{-1}$, respectively. Based on this method of analysis, and assuming that electron-dense
301 functional groups are the primary factor in determining ROS quenching, the inhibition capacity of the
302 fractions could be expected in this order: HPO>C>TPI. Neither of these methods are expected to
303 conclusively predict the true inhibition potential, given the many additional factors involved with
304 quenching mechanisms.

305 3.2. EfOM composition and effect of membrane fouling

306 To estimate the effect of membrane fouling and cleaning on the retention of fluorophores, 3DEEM
307 spectra of MBR bulk supernatant and permeate were compared (Figure 2). The membranes rejected
308 most compounds from Regions I and II in the three MBR cases studied. This selectivity was apparent

309 in the 3DEEM spectra obtained by subtracting the permeate spectrum from the BSN spectrum. It is
310 likely that most of these aromatic-like fluorophores were associated with organic colloids since they
311 represented 80% of the overall colloidal content. This observation is consistent with a previous study
312 that demonstrated that colloids were major membrane foulants.²³

313



314

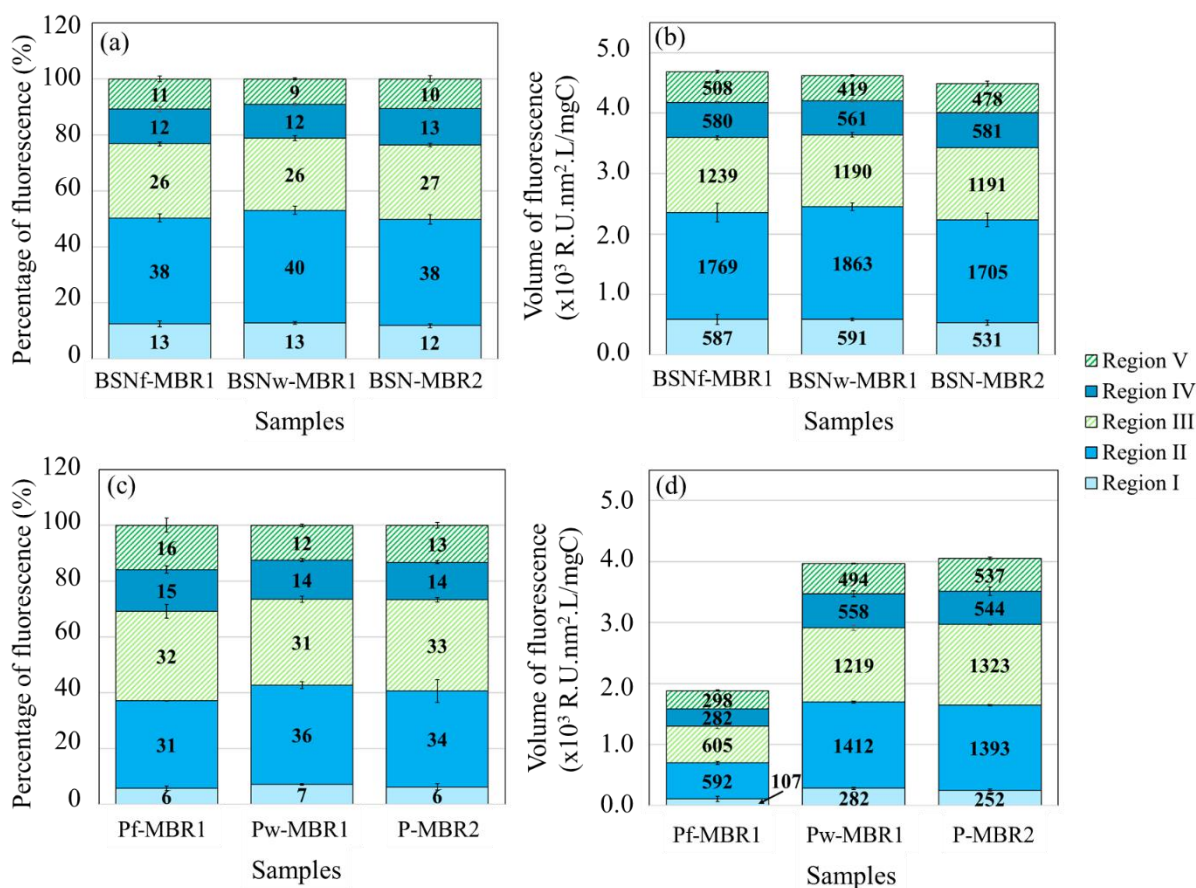
315 Figure 2. Fluorescence spectra of DOM from BSN and EfOM from permeate samples, with I, II, III, IV, V
316 corresponding to Region I (aromatic proteins-like type I), Region II (aromatic proteins-like type II), Region III
317 (fulvic-like), Region IV (SMP-like) and Region V (humic-like). R spectra correspond to the mathematical
318 subtraction of the permeate spectra from the bulk supernatant spectra allowing the identification of compounds
319 retained by the membrane. Note the different color scale for the R spectra.

320

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324

325 Figure 3. Percentage (a, c) and volume (b, d) fluorescence values for bulk supernatant (a, b) and
 326 permeate (c, d) samples.

327

328 Figures 3a and 3c show the fluorophore compositions in EfOM samples as percentages of the different
 329 regions; these data showed a preferential rejection of the fluorophores from Region I and Region II.

330 Indeed, for the three samples, the membrane reduced the fluorescence by 11 ± 2 % in both Region I
 331 and II. This reduction corresponded to an increase of fluorescence percentage of the Regions III and V

332 in the permeate. The relative increase of the humic substance-related fluorophores confirmed that the

333 membrane preferentially retains colloids, since they are typically high molecular weight molecules

334 associated with protein-like fluorophores (Figure 1a).⁵³ Membrane fouling clearly affected the type of

335 fluorophores retained in the MBR (Figure 3b and Figure 3d). The three fouling stages present similar

336 bulk supernatant volumes of fluorescence (Figure 3b) and permeate percentage of fluorescence

337 profiles (Figure 3c), but different volumes of fluorescence in the permeate (Figure 3d). The TOC

338 normalized volume of fluorescence for Pf-MBR1 was reduced by 60% (Figure 3b and Figure 3d),

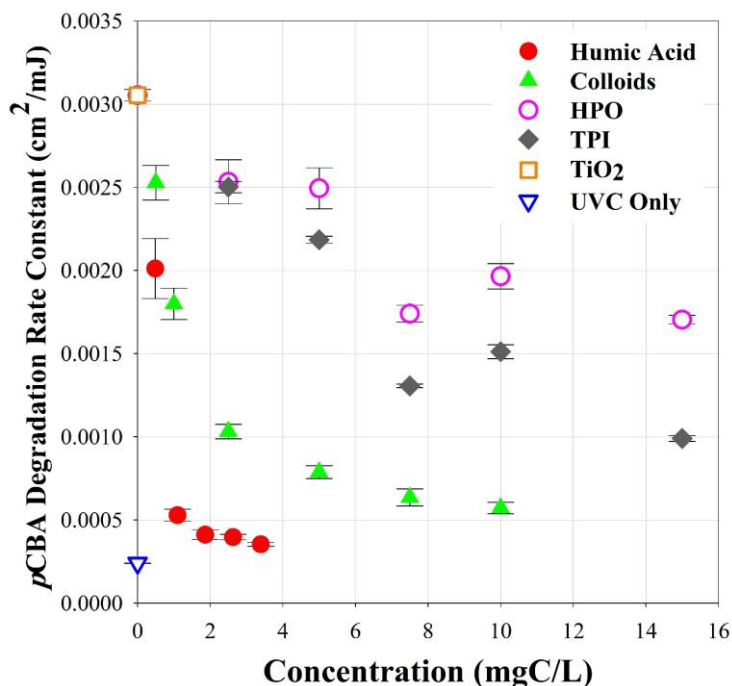
339 while the volume of fluorescence was only reduced by 14% and 10% for P-MBR2 and Pw-MBR1,
340 respectively (Figure 3b and Figure 3d). Membrane fouling therefore has a clear effect on fluorophore
341 quantity, via restricting EfOM permeation (Figure 3b). Indeed, more fluorescent compounds are
342 retained, on a per carbon basis, by a fouled membrane. This result shows that the fouling layer on the
343 membrane surface selectively removes compounds rich in functional groups with high electron
344 density, which are more reactive with ROS than other moieties. Pw-MBR1 and P-MBR2 are therefore
345 expected to quench photocatalysis to a greater extent. This assumption is supported by the SUVA₂₅₄
346 data: values for the Pf-MBR1, Pw-MBR1, and P-MBR2 samples were measured to be 0.8, 2.0, and 2.0
347 L·mg⁻¹·m⁻¹, respectively. Pf-MBR1, having a SUVA₂₅₄ value of 0.8 L·mg⁻¹·m⁻¹, is characterized by
348 non-aromatic organic compounds and therefore fewer potential functional groups reactive with ROS.
349 On the contrary, Pw-MBR1 and P-MBR2, with SUVA₂₅₄ values of 2.0 L·mg⁻¹·m⁻¹, contain more
350 aromatic compounds, which may preferentially compete with ROS.

351 Control of membrane fouling may provide an opportunity to increase photocatalysis process efficiency
352 by regulating the chemical makeup and concentration of EfOM. Less frequent cleaning events could
353 be ideal, since the fouled membranes provided the highest DOM retention. From the fluorescence
354 volumes, it is expected that TiO₂ photocatalysis would be quenched to a greater extent by Pw-MBR1
355 and P-MBR2, than by Pf-MBR1.

356 3.3. Inhibition of ·OH by DOM Fractions

357 Segregation of MBR DOM into functional categories allowed for a unique examination of the
358 inhibition potential of these functional classes of compounds. Colloidal, HPO, and TPI fractions were
359 each examined for concentration-dependent inhibitory activity. Control tests confirmed the
360 photocatalytic action of TiO₂ and differentiated the role of ROS from the direct photolysis by UV₂₅₄
361 light (Figure S3). The action by UV₂₅₄ alone represented the lower bound of $k_{\text{obs},p\text{CBA}}$, where ·OH
362 radicals were completely quenched by DOM. Likewise, the case of TiO₂ and *p*CBA in pure water
363 served as the upper bound of photocatalytic efficiency, with no interfering quenching agents. The
364 $k_{\text{obs},p\text{CBA}}$ values plotted in Figure 4 showed that of the three DOM fractions, colloids exerted the
365 strongest inhibition by far. The corresponding k'_{obs} (s⁻¹) data is shown in Figure S4. The TPI and HPO

366 portions were similar in their effect on $k_{\text{obs},p\text{CBA}}$, and exerted mild inhibition at low TOC
367 concentrations. Interestingly, for both TPI and HPO, the $k_{\text{obs},p\text{CBA}}$ increased from 7.5 to 10 mgC/L. This
368 increase in photodegradation efficacy was surprising but not unprecedented; it was recently reported
369 that Natural Organic Matter (NOM) actually enhanced the TiO_2 -driven photodegradation of
370 carbamazepine, pharmaceutical compound, at specific TiO_2 :NOM ratios, by up to 8%.⁷⁶ Favorable
371 NOM-carbamazepine interactions explained the increased effectiveness; these interactions draw the
372 compound closer to the active surface sites of TiO_2 , where $\cdot\text{OH}$ are present at higher concentrations.
373 The colloidal fraction did not increase the photoactivity at any concentration. Examination of the
374 inhibition profiles of the three DOM fractions in the context of 3DEEM analysis (Figure 1) suggested
375 that the quenching action of the DOM fractions is correlated to higher concentration of colloids, which
376 are characterized by a higher proportion of fluorescence in Region I and Region II (Figure 1a). This
377 observation suggests that despite higher volumes of fluorescence, HPO and TPI are less potent
378 inhibitors of photocatalysis than the colloids. The surface interactions, and therefore inhibition
379 mechanism, of the colloids with the TiO_2 surface could be fundamentally different from that of the
380 HPO and TPI fractions, because the colloidal fraction was not segregated based on surface character,
381 but rather by size only. Control of membrane surface properties and fouling could reduce the colloidal
382 content—much of which consists of high molecular weight molecules that can be preferentially
383 retained—in EfOM and thereby mitigate the quenching of photocatalytic processes by DOM.²³



384

385 Figure 4: *p*CBA degradation rate constants in the presence of 5 mg/L TiO₂ and various concentrations
 386 of colloids, TPI, HPO, and HA are depicted here. The rate constant for *p*CBA degradation by UVC
 387 without TiO₂ is also shown. Ambient temperature was measured at 24 °C.

388

389 3.4. Inhibition of ·OH by EfOM

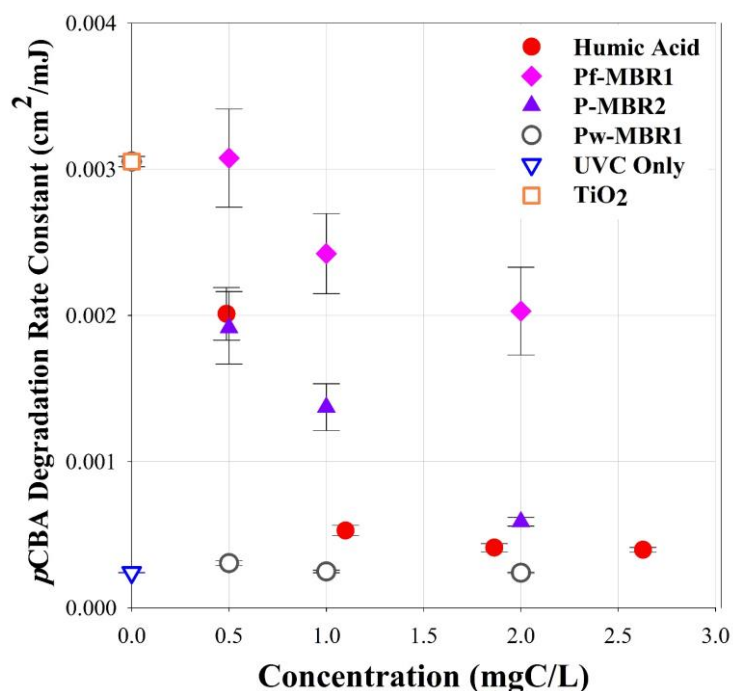
390 The EfOM of the three MBR permeate samples, as described above, was tested for inhibition potential
 391 of ·OH-mediated *p*CBA degradation. The samples were examined on a TOC basis to discern changes
 392 in inhibition potential caused by qualitative differences in EfOM composition. A low concentration of
 393 TiO₂, relative to that used in similar studies on photocatalyst-DOM interactions,^{29, 38, 77, 78} was selected
 394 to avoid the effects of EfOM transformation by oxidation. Hour-long UVC irradiation experiments
 395 with 10 mg/L HA and various concentrations of TiO₂ showed that *p*CBA photodegradation kinetics
 396 were linear for the TiO₂ concentration of 5 mg/L. Tests with TiO₂ concentrations of 100 mg/L or
 397 higher showed accelerating kinetics and suggested that HA was itself being degraded by ·OH radicals
 398 so that its inhibition potential changed with time.

399 The inhibition capacities of MBR EfOM samples were evaluated by measuring $k_{obs,pCBA}$ as a function
 400 of individual EfOM sample concentrations. These rates were calculated across concentrations ranging

401 from 0 to 2.3 mgC/L (Figure 5). The corresponding k'_{obs} (1) data is shown in Figure S5. Comparing
402 $k_{\text{obs,pCBA}}$ values for the same TOC content reveals that the state of membrane fouling drove clear
403 distinctions in inhibitory activity of the EfOM. While it was expected that a fouled membrane would
404 reject more DOM than a clean membrane, the inhibition capacity on a per carbon basis was not
405 known. Here, it was observed that EfOM from a fouled membrane system inhibited the photocatalytic
406 process much less than EfOM from a cleaned membrane. At just 0.5 mgC/L, Pw-MBR1 quenched the
407 photocatalytic process completely, while no quenching was observed by Pf-MBR1 EfOM at the same
408 concentration. This result provides evidence that the changes in EfOM composition caused by
409 membrane fouling; the reduction of colloid concentration and total fluorophores is especially
410 beneficial for photocatalytic operation. 3DEEM confirmed that molecules containing fluorescent
411 groups in Regions I and II impact photocatalytic performance more than other compounds. Qualitative
412 changes in DOM retention by the membrane, therefore, impacted the photocatalytic quenching
413 process. Considering these results in the context of the DOM fractions analysis, retention of organic
414 colloids by the fouled membrane was likely enhanced by the formation of a fouling layer.^{3, 22}
415 Inhibition by P-MBR2, sourced from a membrane at the midpoint between chemical cleanings, was
416 between the two extremes of Pw- and Pf-MBR1, with a ~75% reduction in $k_{\text{obs,pCBA}}$ at 0.5 mgC/L.
417 Alternatively, it may be possible to choose or modify membrane materials to selectively reject the
418 organic colloidal materials regardless of the fouling state. HA served as a reference material, which
419 represents NOM found in drinking water sources more closely than EfOM, and exhibited stronger
420 quenching than the P-MBR2 case but less inhibition than Pw-MBR1. It is noteworthy that HA inhibits
421 TiO₂ driven photocatalysis to a greater extent than EfOM from a fouled MBR on a carbon basis. This
422 finding contradicts a 'common sense' assumption that could be made based solely on TOC values: that
423 photocatalysis would be more applicable for drinking water applications than for WWTP effluent.

424 The 3DEEM analyses (Figure 3) of the MBR EfOM samples predicted that the fouled membrane
425 would reduce the quantity of fluorescent compounds in the EfOM and therefore lead to less inhibition
426 of photocatalysis. However, for cases of similar fluorescence volumes, as for Pw-MBR1 and P-MBR2
427 in particular, the use of 3DEEM did not explain differences in inhibitory action. In these cases, other

428 factors, such as the hydrophobic/hydrophilic character of the EfOM, may have been altered by the
 429 membrane fouling but not detected by 3DEEM or TOC analysis. It is well known that membrane
 430 fouling affects rejection of DOM components^{41, 43, 79} and that the mechanism of action is not simply
 431 size exclusion alone: changes in the surface characteristics (i.e. charge and hydrophobicity), due to
 432 fouling layer formation, are also important.^{3,22}



433

434 Figure 5: *p*CBA degradation rate constants in the presence of various concentrations of HA, effluents
 435 from Pf-MBR1, from Pw-MBR1, and from P-MBR2 with 5 mg/L TiO₂ are depicted here. The rate
 436 constant for *p*CBA degradation by UVC without TiO₂ is also shown.

437

438 3.5. Inhibitory mechanisms for DOM samples

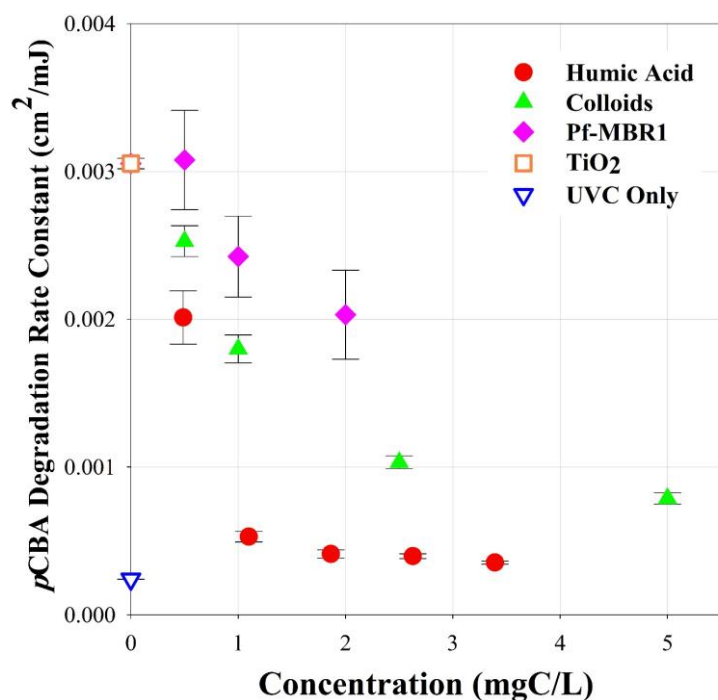
439 Identification of the mechanism of inhibition by DOM on TiO₂ photocatalysis is the key to designing
 440 processes to overcome the problem of ROS quenching. Numerous studies have evaluated the
 441 adsorption interactions of NOM onto TiO₂, fitting experimental findings to Freundlich⁸⁰ or Langmuir-
 442 Hinshelwood^{32, 77, 81} isotherms. Only recently, however, was a model developed that accounted for
 443 both bulk- and surface-phase quenching interactions.²⁹ In their work, Brame et al. experimentally
 444 validated a model that combined a multi-solute Langmuir model⁸² with bulk phase competitive

445 reaction rates by assuming steady-state ROS concentrations.²⁹ Based on this dual-phase model, the
446 mode of inhibition (bulk or surface reactions) was successfully predicted by analysis of the
447 dependency of k_{obs} on TOC. A linear dependence of k_{obs} on TOC implied that inhibition primarily
448 occurred in the bulk phase and surface interactions were unimportant; alternatively, an exponential
449 decay of k_{obs} with increasing TOC indicated that surface sorption and reactions played a significant
450 role in the inhibitory process.²⁹ Note that the aforementioned report used Suwannee River humic acid
451 as an NOM source, which consists of a wide range of molecules;²⁹ applying Brame's model in
452 experiments with fractionated DOM samples is an important extension of the earlier work allowing for
453 a discriminating analysis of inhibition mechanisms across the DOM spectrum. Here, all experiments
454 were performed with the same probe compound, photocatalyst concentration, and UV₂₅₄ lamp, so
455 normalization of $k_{\text{obs},p\text{CBA}}$ was not necessary. The inhibition profile for HA was non-linear and
456 therefore depended on surface interactions, in line with previous reports for TiO₂ inhibition by
457 NOM.^{29, 38, 83, 84} Upon examination of the inhibitory profiles of the MBR effluents, trends for Pf-MBR1
458 and P-MBR2 were noted to be nearly linear, whereas Pw-MBR1 showed an exponential relationship.
459 These observations suggest that the membrane fouling layer played a critical role by rejecting DOM
460 that adsorbs favorably onto the surface of TiO₂, thereby exerting a strong quenching effect on
461 photocatalytic processes. These observations correlate well with the observed inhibition profiles of the
462 fractionated DOM.

463 As discussed, the colloidal fraction of BSN DOM exerted the strongest inhibitory action of any of the
464 fractions (Figure 4). The $k_{\text{obs},p\text{CBA}}$ inhibition profiles of the DOM fractions reveal that the colloids
465 quenched the photocatalytic process via sorption onto the TiO₂ surface and reacting with surface-
466 bound $\cdot\text{OH}$. The HPO and TPI fractions, however, displayed a linear dependence—if the spurious
467 enhancement of $k_{\text{obs},p\text{CBA}}$ at the 10 mgC/L mark is neglected—on TOC. The HPO and TPI samples,
468 therefore, primarily reduced $k_{\text{obs},p\text{CBA}}$ through bulk phase reactions limited by diffusion and relative
469 reaction rates. Note that these remarks on quenching mechanisms are generalizations: even the
470 fractionated DOM samples contain a wide variety of molecules, each with specific adsorption
471 affinities and reaction rates. Still, results of both fractionation and membrane fouling conditions

472 showed significant changes to inhibitory action of DOM. The inhibitory action of the colloidal fraction
473 was particularly interesting, given the lack of inhibitory action by effluent from the fouled membrane.
474 These observations taken together in Figure 6 (data replotted from Figures 4 and 5) suggest that fouled
475 membranes reject key organic colloids that would otherwise adsorb strongly to TiO₂ surfaces and
476 greatly reduce photodegradation rates. The corresponding k'_{obs} (s⁻¹) data is shown in Figure S6. The
477 prospective utility of a membrane for pretreatment is clearly demonstrated by these results: if a
478 membrane can be selected or optimized to reject problematic colloids, photocatalysis may indeed be
479 effective for disinfection of MBR effluent.

480



481

482 Figure 6: $k_{\text{obs},p\text{CBA}}$ inhibition profiles of HA, Pf-MBR1, and the colloidal fraction. Data from Figures 3
483 and 4 are used here.

484

485 4. Conclusions

486 The challenge of unwanted ROS-DOM reactions has long plagued photocatalysis, particularly for
487 applications dealing with high TOC concentrations such as in a typical MBR effluent. 3DEEM can be

488 used to predict the inhibitory effects of DOM composition, and the experiments shed new light on the
489 quenching of photocatalysts by DOM. First, the total fluorescence volume correlated well with the
490 extent of photocatalytic inhibition on a carbon basis, further the DOM fractionation demonstrated that
491 the colloidal fraction of DOM exerted stronger quenching action than HPO and TPI. The membrane
492 fouling status showed that fouled membrane showed very little inhibitory action compared to permeate
493 from clean and moderately fouled membranes. In fact, DOM from fouled membrane appeared to
494 quench $\cdot\text{OH}$ primarily via bulk-phase scavenging, whereas DOM from a clean membrane showed an
495 inhibition profile consistent with surface-phase reactions,²⁸ suggesting that the membrane fouling layer
496 rejected materials that would otherwise adsorb strongly to the TiO_2 surface. To enhance
497 photocatalysis efficiency, it might be possible to select a membrane with a “built-in” selectivity
498 similar to that of the fouled membrane in order to remove the problematic colloidal fraction. Analysis
499 of the inhibition profiles of the EfOM described here suggests that for the operation of a PMR a trade-
500 off can be made between the operational pressure and the photocatalytic efficiency; by reducing the
501 (chemical) cleaning frequency and thereby maintaining a minimal level of fouling, inhibition of
502 photocatalysis by organic colloidal inhibitors would be mitigated at a cost of higher trans-membrane
503 pressures. Further, the surface coverage of TiO_2 on PMRs can be tuned to optimize photocatalyst
504 surface area⁸⁵ and may not be limited to the DOM: TiO_2 ratios explored here.

505 Further research on the fundamental surface interactions between these organic colloidal materials and
506 photocatalyst or membrane surfaces should be pursued in order to develop mitigation strategies for
507 DOM-related ROS inhibition. Specifically, the assessment of the potential effects of the hydrophilic
508 fraction and dissolved ions (i.e., multivalent cations and halides), which were not retained by the
509 fractionation processes, should be examined. The results of the present study may be applicable to the
510 use of photocatalytic materials in systems containing other DOM sources, therefore additional
511 investigations on systems such as potable water supplies or industrial waste streams would be timely
512 and important.

513

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521

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