Hybrid ferrihydrite-MF/UF membrane filtration for the simultaneous removal of
dissolved organic matter and phosphate

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Abstract

Dissolved organic matter (DOM) and phosphorus promote microbial re-growth in
water distribution networks. Ferrihydrite (Fh) has a high adsorption affinity with
DOM and phosphate. Hence, a lab-scale unit of the hybrid Fh-MF/UF membrane
filtration system was used to evaluate membrane fouling and the removal efficiency
of DOM and phosphate. Suwannee River natural organic matter (SRNOM) was used
as a surrogate for DOM in natural water. The Fh-membrane system demonstrated
removal rates of dissolved organic carbon (DOC), UV₂₅₄ and phosphate up to 50%,
80% and 90%, respectively, at the Fh dose of 17.5 mg/L. The effect of phosphate on

the removal of DOM was different without or with the addition of Fh; namely, phosphate increased the DOM removal without Fh by interacting with the UF membrane made of regenerated cellulose (RC), but phosphate decreased the DOM removal by Fh due to the strong affinity of phosphate with Fh. Size exclusion chromatography revealed that phosphate mainly competed against smaller DOM molecules for Fh adsorption sites. Although the addition of Fh caused only a moderate flux decline with the RC membranes, the deposition of positively charged Fh on the surface of a negatively charged high-flux membrane, i.e., polyethersulfone (PES), caused a rapid decline of the permeation flux.

Keywords: adsorption; dissolved organic matter (DOM); ferrihydrite; low pressure membrane filtration; membrane fouling.

1. Introduction

Controlling microbial regrowth in water supply networks is a common problem in many water utilities around the world. In the literature, dissolved organic matter (DOM) is considered to be the limiting nutrient for bacterial regrowth (Hijnen, 2009). Phosphate is an essential element for the growth, activity and regulation of microorganisms, including bacteria. No biofouling was observed at low phosphate concentrations in a reverse osmosis (RO) process, even at a high DOM concentration (Vrouwenvelder et al., 2010). Hence, phosphorus has also been reported to be the rate-limiting factor of microbial growth in water supply systems (Lehtola et al., 2002).

45 Both DOM and phosphorus are present in most drinking water sources. Therefore,
46 minimizing both inorganic nutrients (phosphate) and DOM is an effective strategy for
47 controlling microbial growth in water supply networks.

48 Chemical coagulation is often applied prior to sand filtration or membrane
49 filtration to enhance DOM removal in drinking water treatment. Activated carbon
50 adsorption is also adapted to further remove DOM. However, DOM removal rates by
51 these methods remain moderate due to the heterogeneity of DOM. The removal
52 capacity of activated carbon for DOM remains low to moderate due to the larger
53 molecular sizes of DOM compared to the pore sizes of activated carbon (Lin et al.,
54 1999). Ferrihydrite (Fh) is an amorphous iron oxide particle (IOP) that has a large
55 surface area and a high adsorption capacity for the phosphate, arsenate and organic
56 matter present in soils, sediments and aquatic systems (Antelo et al., 2010). DOM can
57 adsorb onto both crystallized, e.g., hematite and goethite, and amorphous IOP
58 surfaces by ligand exchange between the acidic carboxylic and the phenolic groups of
59 DOM and the hydroxyl groups of IOP to form inner-sphere complexes or by
60 physisorption to form outer-sphere complexes (Gu et al., 1994; Ha et al., 2008).
61 Numerous organic contaminants, including pesticides, herbicides and organic nutrients,
62 have been reported to be efficiently removed by Fh from natural soil and waters
63 (Jambor et al., 1998). On the other hand, the phosphate ions may form bidentate
64 complexes with adjacent sites on the Fh (Gimsing and Borggaard, 2007). Therefore,
65 Fh is expected to remove both phosphate and DOM simultaneously to control
66 microbial re-growth in water supply networks. However, Fh must be separated from

67 water after adsorption of DOM and phosphate.

68 Low-pressure membrane filtration processes such as microfiltration (MF) and
69 ultrafiltration (UF), have many advantages, such as high removal efficiency of
70 suspended solids and smaller footprints; therefore, they are widely used in drinking
71 water treatment for the removal of pathogens and suspended particulate matter (Guo,
72 et al., 2010). However, low-pressure membrane filtration processes are not effective
73 in removing inorganic nutrients and DOM, which can support bacterial regrowth and
74 can form disinfection by-products (DBPs) (Chong et al., 2009; Richardson, 2003).
75 Hence, a hybrid Fh-adsorption and MF/UF membrane filtration system is an attractive
76 process for the simultaneous removal of nutrients, i.e., phosphate and DOM, and
77 particulate matter, which is consistent with the recent trend of integrating pretreatment
78 processes to low-pressure membrane systems (Huang et al., 2009). Cui and Choo
79 (2013) used an IOP column as a pretreatment, before the use of a UF membrane, to
80 control DOM. The integrated IOP/UF system promoted DOM removal and controlled
81 membrane fouling. However, a hybrid system of Fh adsorption integrated into a
82 MF/UF membrane filtration system for the simultaneous removal of DOM and
83 phosphate has not yet been investigated.

84 Therefore, the aim of this study was to investigate the simultaneous removal of
85 DOM and phosphate by a hybrid Fh-MF/UF system and to assess the effect of Fh
86 addition on membrane fouling. Dead-end filtration experiments with and without the
87 addition of Fh were performed to filter feed waters containing Suwannee River
88 natural organic matter (SRNOM) and phosphate. The removal efficiencies of

89 SRNOM and phosphate and the permeation flux were monitored for different types of
90 MF and UF membranes.

91

92 **2. Materials and methods**

93 **2.1 Preparation and characterization of ferrihydrite (Fh)**

94 The 2-line Fh was synthesized following the method reported by Patrizia et al.
95 (2001). The concentration of Fh was measured by inductively coupled plasma atomic
96 emission spectroscopy (ICP-AES, Optima 3000DV, PerkinElmer Inc., USA), if
97 necessary, after dilution. Surface area and pore size distribution were characterized by
98 the nitrogen adsorption method (Belsorp mini-II, Bel Japan Inc.), and the results are
99 presented in Table 1. Scanning electron microscopy (SEM) (VE-8800, Keyence Corp.,
100 Osaka, Japan) revealed that the mean particle size of Fh was $8 \pm 2 \mu\text{m}$ (Fig. 1).

101

102 **2.2 Feed water**

103 Suwannee River natural organic matter (SRNOM, RO isolation, 1R101N),
104 purchased from the International Humic Substances Society (IHSS, St. Paul, MN,
105 USA), was dissolved in Milli-Q water. The solution pH was adjusted to 7.5 by adding
106 NaOH while being mixed using a magnetic stirrer. Afterwards, the solution was
107 filtered through a 0.45- μm PTFE membrane (JH, Millipore, USA). The stock
108 SRNOM solution had a DOC concentration of 100 mg-C/L and was stored at 4 °C in
109 the dark until use. In the membrane experiments, the initial concentration of DOC was
110 kept at 2.5 to 2.8 mg/L based on the water quality of a river that is the source of water

111 supply in Tokyo. A 100 mg/L phosphate stock solution was prepared by dissolving
112 K_2HPO_4 chemical reagents and then added into the diluted SRNOM solution for the
113 Fh-membrane filtration experiments.

114

115 **2.3 Membrane properties**

116 Three different membranes were used in this study to investigate the effect of the
117 membrane characteristics on the performance of the hybrid Fh-MF/UF process. The
118 two UF membranes were made of regenerated cellulose (RC) (YM-100; Millipore
119 Corp., MA, USA) or polyethersulfone (PES) (PBHK; Millipore Corp., MA, USA),
120 while the MF membrane was made of mixed cellulose esters (VCWP; Millipore Corp.,
121 MA, USA). The membrane properties are presented in Table 2. The UF membranes
122 had the same nominal molecular-weight cut-off (MWCO), but the PES membrane is
123 negatively charged at neutral pH, while the RC membrane is slightly positively
124 charged. The RC and VCWP membranes are hydrophilic, whereas the PES membrane
125 is hydrophobic with a contact angle greater than 50°.

126

127 **2.4 Membrane filtration process**

128 A hybrid membrane filtration was performed in a batch stirred cell with a full
129 capacity of 70 mL as shown in Fig. 2. A disc filter having an effective filtration area
130 of 13.4 cm² was installed in the filtration cell. Prior to use, each membrane was placed
131 in Milli-Q water for 24 h to remove wetting agents and production residues.
132 Membrane filtration was performed at a constant trans-membrane pressure (TMP) of

133 60 kPa for the UF membranes and at 30 kPa for the MF membrane, which was
134 monitored by a digital pressure gauge. The filtrate flux was calculated by weighing
135 the permeate water using a digital balance connected to a personal computer. A new
136 membrane was used for each experiment. At the beginning of each filtration
137 experiment, 70 mL of Fh solution (50 mg-Fe/L) was added into the filtration cell, and
138 then the filtration was continued until a predetermined volume of permeate, usually
139 900 mL, was obtained. The stirring rate was maintained at 600 rpm to minimize cake
140 formation due to Fh deposition. The Reynolds number was calculated as 19800,
141 which is in the range of complete turbulent flow and is comparable to the practical
142 operational condition of cross-flow membrane filtration processes. The solution pH
143 was adjusted to 7.1 with the addition of HCl or NaOH.

144

145 **2.5 Analytical methods**

146 The molecular weight (MW) distribution of the DOM was analyzed by
147 high-performance size exclusion chromatography (HP-SEC) using LC-10ADvp
148 (Shimadzu Corp., Kyoto, Japan) with an online diode array detector and a Protein
149 Pak60 column (Waters Corp., USA), as described in Yang et al. (2012). This system
150 can analyze DOM between 0.1 and 100 kDa, which is below the molecular-weight
151 cut-off of the UF membranes. The dissolved organic carbon (DOC) was measured
152 using a TOC-5000A (Shimadzu Corp., Kyoto Japan) analyzer, and the phosphate
153 concentration was measured using a DR/890 portable colorimeter (Hach Company,
154 Colorado, USA) with a detection limit of 0.03 mg/L as PO_4 , which is equivalent to

155 0.01 mg/L as P.

156

157 **3. Results and discussion**

158 **3.1 Removal of SRNOM and phosphate using a UF (RC) membrane with and** 159 **without Fh**

160 As reported in our previous study (Yang et al., 2012), adsorption of DOM onto Fh
161 achieved equilibrium within 5 min. In the hybrid Fh-membrane filtration system used
162 in this study, the hydraulic residence time in the filtration cell was more than 8 min,
163 and the Fh suspension was completely mixed by a magnetic stirrer. Hence, the DOM
164 adsorption onto Fh was expected to be in equilibrium in all experiments.

165 The changes of the normalized flux during filtration of the solutions containing
166 only SRNOM or SRNOM and phosphate are shown in Fig. 3. The addition of Fh
167 slightly decreased the fluxes of the RC UF membrane, but not significantly. The mean
168 particle size of Fh, i.e., $8 \pm 2 \mu\text{m}$ as described in Section 2.1, was approximately 400
169 times greater than the membrane pore diameter of 14.3 nm, which was estimated by
170 the following equation (Howe and Clark, 2002):

$$171 \quad d = 0.09(\text{MWCO})^{0.44}$$

172 where d is the membrane pore diameter in nanometers, and MWCO is in Daltons
173 (Da). Although Fh particles are too large to enter and block the pores, they might
174 deposit on the membrane surface and partially plug the large pores. However, there
175 was no evidence of the fast flux decline in the initial stage, which eliminates the
176 possibility of pore blocking.

177 The apparent DOC removal, i.e., the removal rates against DOC concentration in
178 the feed water, by the RC membrane alone was about 30% at the beginning of
179 filtration, but reduced to about 20% at the end of filtration due to the increase in the
180 DOC concentration in the filter cell (Fig. 4 (a)). It is noteworthy that the addition of
181 phosphate increased the DOC removal in the initial stage of filtration up to 200 L/m².
182 There is no direct evidence showing the interaction between phosphate and DOM
183 because both SRNOM and phosphate are negatively charged and because little
184 removal of phosphate was observed by the RC membrane alone, while about 50% of
185 DOC was removed (Fig. 4(a)). Alternatively, phosphate could be sorbed onto the RC
186 membrane surface, resulting in a more negatively charged membrane surface at the
187 initial state of filtration (Song et al., 2011). This situation of phosphate adsorption
188 seems to be more reasonable, as it is known that phosphorus reacts with cellulose in
189 the paper making process (Ly and Brouillette, 2013). Phosphate adsorption was also
190 supported by a slight removal of phosphate at an early state of filtration (Fig. 5(a))
191 and the changes of the zeta potential on the RC membrane surface, as presented in
192 Table 3. The surface charge of RC membrane changed from slightly positive to
193 negative, which enhanced the electrostatic repulsion between SRNOM and the
194 membrane surface.

195 UV₂₅₄ indicates UV-absorbing DOM including aromatic DOM. The initial
196 removal rate of UV₂₅₄ by the RC membrane was about 70% (Fig. 4 (b)), which was
197 twice as high as the removal rate of DOC. The UV₂₅₄ removal rates decreased rapidly,
198 but maintained a higher removal rate than the DOC removal at the end of filtration.

199 The addition of phosphorus did not change the UV_{254} removal rate, which indicated
200 that molecular size, rather than electric charge on the filtration of aromatic DOM,
201 determined the removal rate. Hence, the high removal rate of UV_{254} indicated that the
202 UV_{254} -absorbing molecules were comparatively larger than the average DOM size as
203 measured by DOC. The Fh addition further increased the UV_{254} removal rate, possibly
204 due to ligand exchange between the carboxylic and phenolic groups of the DOM and
205 the hydroxyl groups of the hydrated Fh surface (Yang et al., 2012).

206 Phosphate adsorbs on Fh mainly by exchange with hydroxyl groups, where the
207 singly coordinated hydroxyl groups on the Fh surface are replaced by phosphate,
208 forming binuclear surface complexes (Borggaard et al., 2005). The inner-sphere
209 complex of phosphate with Fh can be formed at pH 4–9.5 (Arai and Sparks, 2001).
210 The strong affinity of phosphorus onto Fh was indicated by the phosphate removal
211 rate of more than 90% up to a filtered volume (FV) of 300 L/m² (Fig. 5 (a)), giving
212 the permeate concentration of less than 0.03 mg-PO₄/L or 0.01 mg-P/L, which is low
213 enough to suppress bacterial regrowth (de Vet et al., 2012).

214 The strong affinity of phosphate with Fh interfered with the SRNOM adsorption
215 onto Fh, as shown by q_v , which is the cumulative removal of DOC per unit weight of
216 Fh (Fig. 5 (b)). The phosphate addition significantly reduced the adsorbed amounts of
217 DOM from 400 to 270 mg-C/g-Fe at the end of filtration by competing with DOM
218 adsorption onto Fh. In turn, the adsorbed DOM blocked some surface sites of Fh and
219 competed for the binding sites against phosphate (Fig. 5 (a)); as a result, the removal
220 rate of phosphate decreased with increasing FV (Geelhoed et al., 1998; Antelo et al.,

221 2007; Weng et al., 2008). The phosphate concentration of 0.48 mg/L in this study can
222 be found in eutrophic water resources with rather high DOC; hence, we need to pay
223 attention to the ratio of DOC and phosphate in the application of the hybrid
224 Fh-membrane filtration process.

225 The HP-SEC analysis with SRNOM revealed three peaks of aromatic DOM that
226 can be measured by UV_{254} absorbance, and the rejection rates of these peaks during
227 the course of filtration is given in Table 4. The addition of phosphate in the absence of
228 Fh slightly increased the removal rates of the three DOM peaks at a FV of 18.6 L/m²,
229 which were more pronounced at a FV of 186 L/m², at which the rejection rate of the
230 DOM peak of 3140 Da increased by 40%. These results are in agreement with the
231 increased DOC removal rates by phosphate addition as shown in Fig. 4 (a), but are not
232 in agreement with the UV_{254} removal shown in Fig. 4(b). This may be because the
233 HP-SEC column used in this study can separate and detect only small DOM
234 molecules, which might comprise only a small fraction of UV_{254} -absorbing DOM.
235 After the addition of Fh, the DOM peak removal rates slightly increased by phosphate
236 addition at the beginning, i.e., FV 18.6 L/m², but decreased at FV 186 L/m² (Table 4).
237 The decrease was not significant at 3140 Da, but more obvious by about 30% at 1770
238 Da and 970 Da at FV 186 L/m² in the hybrid Fh-RC system. This 30% decrease in the
239 DOM removal was caused by competition against phosphate, which means that
240 phosphate competed against the smaller DOM molecules than ca. 2000 Da for the
241 adsorption sites on Fh, but did not compete to against the DOM molecules larger than
242 ca. 2000 Da.

243 **3.2 Comparison between RC and PES UF membranes**

244 The mixed solution of SRNOM and phosphate was filtered through a PES
245 membrane (Table 2) at the same TMP of 60 kPa as in the filtration by the RC UF
246 membrane. The PES membrane had a higher initial flux of 621.6 L/(m² h) than that of
247 the RC membrane (288.4 L/(m² h)). As shown in Fig. 6, the flux decline caused by the
248 addition of Fh was more significant with the PES membrane than that with the RC
249 membrane; that is, the filtrate flux of the Fh-laden feed water decreased rapidly at the
250 beginning of the filtration and became almost steady when the flux approached to
251 about 60% of the initial flux with the PES membrane. The flux decline of Fh-RC,
252 Fh-PES, RC alone and PES alone were 25%, 50%, 10% and 20%, respectively, at FV
253 670 L/m². The surface of the PES membranes was more negatively charged than that
254 of the RC membranes (Table 2). Hence, the PES membrane has a strong attraction
255 with Fh, which is slightly positively charged at pH 7.0 with a zeta potential of 1.8 ±
256 0.4 mV as determined by an automated electrophoresis analyzer. In addition to the
257 higher initial flux, the electrostatic attraction of Fh with the PES membrane might be
258 the cause of the rapid reduction of the flux. The concentration of Fh in the filtration
259 cell reduced from 50 mg-Fe/L at the beginning of filtration to 18.2 mg-Fe/L at the end
260 of filtration in the Fh-PES membrane system, but the concentration of Fh did not
261 significantly change in the cell after the RC membrane filtration. This result indicated
262 that, though Fh size is large enough not to cause pore blocking, a large amount of
263 deposition on the PES membrane caused cake fouling that led to the flux reduction by
264 50%.

265 The addition of Fh significantly improved the removal efficiency of DOC, UV₂₅₄,
 266 and phosphate by both the RC and PES membranes, but in different manners (Figs. 7
 267 and S1 in Suppl. Info.). The PES membrane alone removed only small amounts of
 268 DOC and UV₂₅₄ compared to those of the RC membrane. Despite the same nominal
 269 MWCO of 100 kDa provided by the manufactures, RC membranes often have tighter
 270 pores than PES membranes (Lee et al., 2008). Hence, the addition of Fh significantly
 271 increased the initial removal rates of DOC and UV₂₅₄ by the PES membrane; the
 272 removal rates diminished rapidly as the filtration volume increased. On the contrary,
 273 the increase of DOC and UV₂₅₄ removal by the RC membrane was moderate, and thus
 274 the decline in the removal rates was relatively slow. The deposition of a large amount
 275 of Fh and formation of a high density cake layer on the PES membrane surface might
 276 have also decreased the removal rate of DOM by Fh adsorption.

277 The specific cake resistance, α , is defined by the following equation as the cake
 278 resistance (R_c) normalized by the accumulated cake mass per unit area of a membrane
 279 (Lee et al., 2000):

$$280 \quad \alpha = \frac{R_c}{\left(\frac{M}{A}\right)}$$

281 where M is the mass of the cake deposited on the membrane surface, A is the
 282 effective area of the membrane. The specific cake resistances of RC and PES
 283 membranes were 6.56×10^{14} and 1.20×10^{14} m/kg, respectively. It is noteworthy that,
 284 despite the larger amounts of Fh deposition, the specific cake resistance was lower for
 285 the PES membrane than for the RC membrane.

286 As shown in Fig. 8 (a), the cumulative DOC removal per unit amount of Fh (based
287 on the initial Fh amount in the filtration unit) was higher in the hybrid system of the
288 RC membrane than that of the PES membrane. However, the cumulative adsorption
289 of phosphate was nearly the same with the RC and PES membranes (Fig. 8 (b)). This
290 difference may be due to the strong affinity and smaller size of phosphate than
291 SRNOM, making it faster to adsorb onto the Fh deposited on the membrane surface.
292 Hence, it can be concluded that the deposition of Fh on the membrane surface
293 significantly affected the adsorption of DOM, which was less preferable to be
294 adsorbed onto Fh than phosphate.

295 **3.3 Comparison between UF (RC) and MF (VCWP) membranes combined with** 296 **Fh**

297 The SRNOM solution was used to compare the performance of the Fh-UF
298 (operated at a TMP of 60 kPa) and Fh-MF (TMP of 30 kPa) systems. As shown in Fig.
299 9, the addition of Fh did not significantly exacerbate fouling in the MF and UF (RC)
300 membranes. This indicated that, when the initial fluxes were nearly the same (RC:
301 288.4 and MF: 306.2 L/ (m² h)), the rates of flux decline caused by Fh deposition
302 were also the same for the membranes without the effect of electrostatic attraction.
303 Unlike the UF membranes, MF membrane alone cannot remove DOM from the feed
304 water. However, Fh addition increased the removal rates of DOC and UV₂₅₄ to 30%
305 and 90%, respectively, by the MF membrane (Fig. S2, Suppl. Info.). It is noteworthy
306 that the DOC and UV₂₅₄ removal rates by the hybrid Fh-MF system remained higher
307 than the Fh-PES system, indicating that maintaining the suspended state of Fh, rather

308 than the membrane pore sizes, is critically important to obtain a higher DOM removal
309 rate in the hybrid Fh-membrane filtration system.

310

311 **4. Conclusions**

312 1. Although the membranes used in this study had moderate (RC) to low (PES and
313 MF) removal rates of DOM, the addition of Fh into the filtration cell increased DOM
314 removal, while simultaneously achieving high removal rates of phosphate.

315 2. Due to high affinity of phosphate with Fh, phosphate interfered with DOM
316 adsorption onto Fh. It was found by HP-SEC analysis that phosphate competed
317 against DOM molecules smaller than ca. 2000 Da for the Fh adsorption sites. In
318 contrast, without Fh, the addition of phosphate increased the DOM removal by the RC
319 membrane by increasing the negative charge of the membrane.

320 3. The flux decline with the RC and MF membranes was only modest, whereas it was
321 significant with the PES membrane. The PES UF membrane was prone to Fh cake
322 fouling due to a high flux and the strong negative charge that caused the deposition of
323 positively charged Fh on the membrane surface. Due to the Fh deposition during the
324 course of filtration, the DOM removal rate was also rapidly decreased with the PES
325 membrane. Hence, ensuring that Fh remained suspended by stirring during filtration
326 was found to be the key to maintaining high DOM and phosphate removal rates and to
327 prevent flux decline.

328 4. Although the hybrid Fh-UF/MF system can be used for the simultaneous removal
329 of DOM and phosphate, we should choose the membrane type and set a filtration flux

330 to prevent Fh deposition on the membrane surface. Among the three membranes used
331 in this study, RC UF membrane was the best because of high DOC removal and
332 moderate membrane fouling. We should also pay attention to the competition between
333 DOM and phosphorus for the application of the system to various types of water
334 resources.

335

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340

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Table 1. Characteristics of synthesized ferrihydrite (Fh).

Surface area (m ² /g)	Pore volume (cm ³ /g)		Pore size (nm)	
	BET equation	BJH equation	BET equation	BJH equation
314.2	0.180	0.194	2.32	2.42

IUPAC classification: < 2 nm:micropore, 2-50 nm: mesopore, > 50 nm: macropore

Table 2. Properties of the membranes. (Millipore Corp.)

	MWCO (kDa)	Pore diameter (nm)	ξ -potential ^b (mV)	Contact angle (°)	Pure water permeability at 25 °C (L/(m ² h kPa))
UF-RC	100	19.4	1.96 ± 0.5	26 ± 3	5.05 ± 1.0
UF-PES	100	n/a	-15.1 ± 0.8	56 ± 3	10.53 ± 0.5
MF-VCWP	-	100 ^a	n/a	19 ± 3	10.87 ± 0.5

^a Nominal pore size, ^b ξ -potential was measured at pH 7 in 10 mM KCl (Burns and Zydney, 2000),
n/a denotes data not available.

Table 3 Zeta (ξ -) potential of UF-RC membrane in Milli-Q water and in phosphate solution

Conditions	ξ -potential ^b (mV)
RC membrane in Milli-Q water	1.96 ± 0.5
RC membrane in 0.5 mg/L phosphate solution	-5.89 ± 0.5

Background solution for ξ -potential measurement was 10 mM NaCl at pH 7.01

Table 4. Removal rates of DOM with different molecular weights.

MW peak (Da)	RC (filtered volume, L/m ²)				RC + Fh (filtered volume, L/m ²)			
	DOM		DOM + PO ₄		DOM		DOM + PO ₄	
	18.6	186	18.6	186	18.6	186	18.6	186
3140	79.6%	26.6%	84.9%	69.1%	94.9%	94.8%	97.8%	91.2%
1770	44.9%	1.0%	51.4%	15.6%	70.1%	37.5%	73.5%	5.8%
970	19.7%	0.5%	32.5%	11.5%	33.6%	27.9%	39.4%	0.1%

Note: The samples were taken at the filtered volume of 18.6 L/m² and 186 L/m².

Fig.1. SEM image of Fh.

Fig.2. Schematic diagram of the membrane system combined with Fh.

Fig.3. Flux decline in RC and hybrid Fh-RC UF membranes in filtration of SRNOM and phosphate solution.

Fh 50 mg-Fe/L, Feed water: SRNOM (DOC: 2.8 mg/L, UV_{254} : 0.088 cm⁻¹, pH=7.1) with or without phosphate (0.48 mg-PO₄ /L); TMP was 60 kPa.

Fig.4. Removal rates of DOC (a) and UV₂₅₄ (b) in RC or hybrid Fh-RC systems. The experimental conditions are the same as those in Fig. 3.

Fig.5. Phosphate removal rates with and without Fh (a) and cumulative DOC removal per unit weight of Fh (b).

The experimental conditions are the same as those in Fig. 3.

Fig.6. Flux decline of mixed solution of SRNOM and phosphate.
 Fh 50 mg/L as Fe; Feed water: SRNOM with phosphate (DOC: 2.5 mg/L, UV_{254} :
 0.086 cm^{-1} , phosphate: 0.5 mg/L, pH=7.1); TMP was 60 kPa.

Fig.7. Comparison of (a) DOC and (b) UV₂₅₄ removal rates by RC and PES membrane systems.

Fh 50 mg/L as Fe; Feed water: SRNOM with phosphate (DOC: 2.5 mg/L, UV₂₅₄: 0.086 cm⁻¹, phosphate: 0.5 mg/L, pH=7.1); TMP was 60 kPa.

Fig.8. Cumulative DOC (a) and phosphate (b) removal by unit weight of Fh combined with RC or PES UF membranes.

Fh 50 mg/L as Fe; Feed water: SRNOM with phosphate (DOC: 2.5 mg/L, UV_{254} : 0.086 cm^{-1} , phosphate: 0.5 mg/L, pH=7.1); TMP was 60 kPa.

Fig.9. Flux decline with UF (RC) and MF membrane in filtration of SRNOM.
 Fh 50 mg/L as Fe; Feed water: SRNOM (DOC: 2.7 mg/L, UV_{254} : 0.096 cm^{-1} , pH=7.1); TMP was 60 kPa for the RC membrane and the 30 kPa for MF membrane.

Ferrihydrite