

Evaluating the performance of gravity-driven membrane filtration as desalination pretreatment of shale gas flowback and produced water

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4 **Evaluating the performance of gravity-driven membrane**
5 **filtration as desalination pretreatment of shale gas flowback**
6 **and produced water**

7

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21 **ABSTRACT**

22 The shale gas extraction industry generates a large quantity of highly contaminated
23 flowback and produced water (FPW), with great impacts on human health and the
24 environment. In this study, gravity-driven membrane (GDM) filtration was evaluated
25 over a 612-day period as a pre-treatment of FPW for its subsequent desalination. The
26 various investigated GDM systems showed similar contaminant removal, and their
27 steady-state fluxes (i.e., 0.65-0.82 L/(m²·h)) were not significantly correlated to
28 membrane configurations or to the hydrostatic pressures. The flux decline was
29 primarily due to a reversible resistance, which accounted for a large proportion (>89%)
30 of the total hydraulic resistance. Compared to traditional ultrafiltration, the GDM
31 pretreatment resulted in better desalination performance for the subsequent
32 nanofiltration or reverse osmosis step, which were characterized by higher organic
33 removal and generally higher permeate fluxes. More than 60 bacterial genera and 8
34 eukaryotic genera were detected in the shale gas FPW, with the kingdoms *Alveolata*
35 and *Stramenopiles* (within the eukaryote domains) reported for the first time. The
36 biofouling layer of GDMs had a lower bacterial diversity but a higher eukaryotic
37 diversity than the FPW feed water. The eukaryotic community, including *Alveolata*,
38 *Fungi*, *Stramenopiles* and *Metazoa*, played a major role in the flux behavior.

39 **Key words:** shale gas; flowback and produced water (FPW); gravity-driven membrane
40 (GDM); desalination pretreatment; microbial community

41 **1. Introduction**

42 Shale gas is one of the most rapidly expanding resources in the oil and gas
43 exploration industry, but its extraction is associated with severe environmental
44 problems, including significant freshwater consumption and the complex management
45 of shale gas flowback wastewater. Large volumes of flowback and produced water
46 (FPW) ($\sim 5,200\text{-}25,870\text{ m}^3$ per horizontal well) are typically generated during shale gas
47 extraction [1]. Based on the prediction of shale gas drilling rates in the Haynesville
48 shale (U.S.) and in the Sichuan Basin shale (China), the number of drilling wells will
49 reach a maximum in the next several years [2]. Therefore, the amount of FPW will also
50 reach a peak value and its management is an urgent issue to guarantee favorable
51 economics of shale gas extraction, while protecting human health and environmental
52 resources [3,4]. The situation is complicated by the numerous types of contaminants
53 that have been detected in shale gas FPW and that pose great challenges for the reuse
54 or discharge of these wastewaters [5,6].

55 Several desalination technologies, including reverse osmosis (RO), nanofiltration
56 (NF), forward osmosis, and membrane distillation have been proposed to deal with
57 shale gas FPW, for their reuse or surface water discharge [6-8]. Effective pretreatment
58 is a critical factor influencing the sustainable operation of these desalination processes,
59 and it can be accomplished using low-pressure membrane (i.e., ultrafiltration (UF) and
60 microfiltration (MF)) [6,9]. Nevertheless, the appeal of UF pretreatment is limited by
61 its relatively high energy consumption due to operational costs and strategies for
62 membrane fouling mitigation; in contrast, the recently developed gravity-driven

63 membrane (GDM) filtration is typically more favorable than conventional UF [10].
64 GDM filtration has received increasing attention in decentralized water treatment due
65 to its advantages, which include ultra-low hydrostatic pressure (e.g., with height of 0.4-
66 1.0 m) and no need for backwashing [11]; therefore, GDM may be attractive also for
67 FPW.

68 The application of GDM has recently extended from surface water [12] to other
69 sources, including rainwater, wastewater, grey water, and seawater [10]. As opposed to
70 surface water as feed solution [11], the permeate flux values in the GDM filtration of
71 seawater depended not only on the feed water properties, but also on the operating
72 temperature and the hydrostatic pressure [13,14]. With respect to membrane properties,
73 UF membranes rather than MF membranes [14-16] have been usually adopted in GDM
74 systems, with flat sheet membranes a more common configuration than hollow fiber
75 membranes [14,15,17,18]. Together with feed organics and operation conditions,
76 another critical factor affecting the flux stabilization and the general flux behavior
77 during GDM filtration is the composition of the biofouling layer [11,12,19,20].

78 Understanding the nature and the proportion of different microorganisms in the FPW
79 is important to predict the performance of the system and to design suitable mitigation
80 strategies. Despite of high salinities and concentrations of biocides [21] in usual shale
81 gas FPW, more than one-third of the organic substances contained in the FPW are
82 biodegradable, showing the potential of biological treatment in FPW treatment [22].
83 The presence of microorganisms in shale gas FPW causes concern for the safety and
84 performance of the operation, and reports on the compositions of the microbial

85 community have recently increased [23-30]. Published research showed that
86 microorganisms may play a great role in organic removals from shale gas FPW using
87 biological treatment processes, such as biologically-active filtration [8] and sequencing
88 batch reactor-membrane bioreactor process [31]. Based on these previous results, GDM
89 is expected to perform well as desalination pretreatment. However, the compositions
90 and changes of microbial community during GDM filtration of shale gas FPW, as well
91 as the impacts of microorganisms on removals of contaminants, need to be investigated.

92 The composition of shale gas FPW is associated to the complexity of its treatment,
93 compared to more conventional municipal wastewater or other produced water [32],
94 also because FPW water exhibits significant spatial and temporal change [6]. This study
95 aims at evaluating the applicability and performance of GDM as a pretreatment for
96 desalinating shale gas FPW from the Sichuan Basin. Specifically, the objectives of this
97 work are: (a) to examine the influence of hydrostatic pressure and membrane
98 configuration on steady-state flux and hydraulic resistance; (b) to assess the removal
99 behavior of contaminants from shale gas FPW by GDM filtration; (c) to analyze the
100 microbial community composition of the raw shale gas FPW and of the biofouling layer
101 of GDM; (d) to determine the effects of GDM on the desalination performance of NF
102 and RO processes; and (e) to investigate the changes in the performance of the
103 membranes after long-term exposure to shale gas FPW.

104

105 **2. Materials and methods**

106 *2.1. Shale gas FPW and water quality analysis*

107 The shale gas wastewater was collected from a storage tank in Longhui Town,
108 Weiyuan County in the Sichuan Basin, China on December 14, 2016. The storage tank
109 with an effective volume of 10,000 m³ received untreated FPW from horizontal shale
110 gas wells. The samples were collected from mid depth (about 1.5 m below the surface)
111 of the storage tank. The primary water parameters of the raw FPW were summarized
112 previously [33,34]. The permeates from GDM systems were collected every 2-3 weeks
113 for water quality analysis. Total dissolved solid (TDS) and **electrical conductivity (EC)**
114 were measured by an Ultrameter II 6PFC portable multifunctional meter (Myron L
115 Company, Carlsbad, CA, USA). Temperature and pH were measured by using a
116 mercury thermometer and a pH meter (PB-10, Sartorius Scientific Instruments Co., Ltd.,
117 Gottingen, Germany), respectively. Turbidity and alkalinity were determined by a
118 turbidimeter (TL2310, Hach Company, Loveland, USA) and by acid-base indicator
119 titration method, respectively. A UV-Vis spectrophotometer (Orion AquaMate 8000,
120 Thermo Fisher Scientific Inc., MA, USA) was employed to measure UV absorbance at
121 254 nm (UV₂₅₄). The chemical oxygen demand (COD) and dissolved organic carbon
122 (DOC) were monitored using the fast digestion-spectrophotometric method with a 5B-
123 1F(V8) fast digestion meter (Lianhua Environmental Protection Technology Co., Ltd.,
124 Lanzhou, China) and an automatic total organic carbon analyzer (TOC-L, Shimadzu,
125 Japan), respectively. The 15-min silt density index (SDI₁₅) of the GDM permeate and
126 UF permeate were measured as described in detail in ASTM D4189-07 (2014) [35].

127 2.2. UF membranes and GDM setup

128 Two types of commercially available polyvinylidene fluoride (PVDF) UF
129 membranes with different configurations (i.e., hollow fiber and flat sheet) were
130 employed. Outside-in hollow fiber membranes and flat sheet UF membranes were
131 obtained from Litree Purifying Technology Co., Ltd. (Haikou, China) and Tianchuang
132 Waterpure Equipment Co., Ltd (Hangzhou, China), respectively. The two UF
133 membranes had the same nominal molecular weight cut-off of 100 kDa. Each hollow
134 fiber membrane had a single fiber with an outer diameter of 1.8 mm and a length of 18
135 cm, thus, the active filtration area of each hollow fiber membrane was roughly 10 cm².
136 The flat sheet UF membrane was round with a diameter of 23 mm, resulting in an
137 effective filtration area of 4.15 cm². The normalized pure water permeability
138 coefficients (at 20 °C) of hollow fiber and flat sheet membranes were 3.5 and 22.4 L
139 m⁻²h⁻¹kPa⁻¹ (350 and 2240 L m⁻²h⁻¹bar⁻¹). Detailed information about surface
140 physicochemical characteristics of both membranes could be found in our previous
141 study [36].

142 The GDM setup consisted of a raw water tank, a constant-level water tank, and
143 several customized GDM filtration cells, as presented in Fig. S1 (Supporting
144 Information). GDM systems comprising either hollow fiber membranes or flat sheet
145 membranes were deployed for 612 days using the raw FPW as feed solution to evaluate
146 the impact of membrane configuration, using the same pressure head of 0.8 m for the
147 two configurations. Starting from the 100th day of investigation, GDM experiments
148 were also run for 512 days using hollow fiber membranes under different hydrostatic

149 pressures of 40, 120, and 160 mbar (i.e., pressure head, $H = 0.4, 1.2,$ and 1.6 m). As
 150 opposed to the most common configurations of GDM systems [10], in this work the
 151 permeate outlet of the module was connected to an overflow tank using a hose with full
 152 pipe flow and with submerged discharge. According to Bernoulli's equation [37], the
 153 driving force of each GDM test was the water head difference between the water level
 154 in each tank and the permeate outlet of the system into the overflow tank (Fig. S2,
 155 Supporting Information), with the detailed calculation summarized in Section SII [38-
 156 40]. The systems were operated continuously at water temperatures in the range 15-
 157 30 °C (Fig. S3, Supporting Information).

158 2.3. Membrane flux and hydraulic resistance

159 The permeate flux ($L\ m^{-2}h^{-1}$, LMH) observed during GDM experiments was
 160 normalized to that measured at 20 °C to eliminate the influence of temperature, using
 161 Eq. (1):

$$162 \quad J_{20} = (J_T \cdot \mu_T) / \mu_{20} \quad (1)$$

163 where J_{20} (LMH) and J_T (LMH) represent the corrected permeate flux at 20 °C and the
 164 measured permeate flux at the prevailing temperature T (°C), respectively; μ_{20} (Pa·s)
 165 and μ_T (Pa·s) are the water viscosities at 20 °C and at the prevailing temperature T ,
 166 respectively. μ_T (cP, $1\ cP = 10^{-3}\ Pa \cdot s$) was calculated with an empirical relationship [41]:

$$167 \quad \mu_T = 1.784 - (0.0575 \cdot T) + (0.0011 \cdot T^2) - (10^{-5} \cdot T^3) \quad (2)$$

168 The total hydraulic resistance (R_{total}, m^{-1}) was calculated based on Darcy's law:

$$169 \quad R_{total} = TMP / (\mu_T \cdot J_T) \quad (3)$$

170 where TMP is the transmembrane pressure (i.e., hydrostatic pressure head, or height)

171 (Pa). The intrinsic membrane resistance (R_{mem}) was measured using ultrapure water
172 before the FPW was fed into the system. The reversibility of membrane fouling is
173 expressed by the percentage of reversible resistance (R_{rev}) over the total hydraulic
174 resistance (R_{total}). The reversible fouling resistance (i.e., biofouling layer resistance) can
175 be obtained by subtracting the clean membrane resistance (R_{mem}) and the irreversible
176 fouling resistance (R_{irr}) from the total hydraulic resistance (R_{total}).

$$177 \quad R_{\text{total}} = R_{\text{mem}} + R_{\text{rev}} + R_{\text{irr}} \quad (4)$$

178 At the end of operation, the biofouling layer was firstly detached from membrane
179 surface by forward flushing with 100 mL of ultrapure water using a syringe. Then, the
180 cleaned membrane was returned to the GDM system to determine the permeate flux by
181 filtering again the raw FPW. It is assumed that the resistance after flushing was the sum
182 of R_{irr} and R_{mem} [42].

183 *2.4. Scanning electron microscopy (SEM) observation*

184 The membrane samples were used for contact angle measurements and for SEM
185 observation after drying under ambient conditions. The membrane surface morphology
186 was determined with a SU8200 SEM (Hitachi, Japan) after gold-coating by a magnetron
187 ion sputter metal coater device (MSP-2S, IXRF Systems, Inc., Japan), while the cross-
188 section of membrane samples was observed with a SU3500 SEM (Hitachi, Japan) after
189 coating with a sputter coater (Q150R ES, Quorum, UK).

190 *2.5. Microbial community analysis*

191 To explore the reason for flux decline and stabilization in the GDM systems, the
192 biofouling layers of hollow fiber and flat sheet membranes were carefully removed at

193 the end of the experiment for analysis of the microbial community. Meanwhile, the
194 microbial community of the raw shale gas FPW was also analyzed. Genomic DNA
195 (gDNA) of the microbial community in biofouling layer samples and sludge of raw
196 shale gas FPW was extracted, based on the reported method [43]. The purity and the
197 concentration of each DNA sample were measured by a NanoDrop2000 UV-vis
198 spectrophotometer (Thermo Scientific, Wilmington, USA) at wavelengths of 260 nm
199 and 280 nm, respectively. A DYY-6C agarose gel electrophoresis (Beijing Liuyi
200 Biotechnology Co., Ltd., China) was used to determine the integration of the DNA
201 samples. After this step, the 16S rRNA and 18S rRNA genes were amplified by
202 quantitative polymerase chain reaction (PCR) using a GeneAmp® 9700 PCR
203 thermocycler (Applied Biosystems, Foster City, CA, USA) in a 20 µL volume reaction.
204 The universal primer sets 338F (5'-ACTCCTACGGGAGGCAGCAG-3') and 806R (5'-
205 GGACTACHVGGGTWTCTAAT-3') [44] were used to amplify the hypervariable
206 region V3-V4 of the bacterial 16S rRNA genes. The eukaryotic 18S rRNA genes were
207 amplified using primer pairs SSU0817F (TTAGCATGGAATAARRAATAGGA) and
208 1196R (TCTGGACCTGGTGAGTTTCC). The detailed description of the composition
209 of the PCR reaction mixture, the amplification conditions, as well as of the Illumina
210 MiSeq sequencing and sequencing data processing are summarized in [Section SI6](#)
211 ([Supporting Information](#)).

212 Usearch software (version 7.1, <http://drive5.com/uparse/>) was used to group
213 sequences with $\geq 97\%$ (similarity) identity into operational taxonomic units (OTUs).
214 The analyses of microbial community composition, the alpha diversity (e.g., Chao,

215 Shannon, Simpson, ACE, and Coverage) and the beta diversity (i.e., Bray-Curtis
216 distance and Non-Metric Multidimensional Scaling (NMDS)) were performed using
217 the free online Majorbio I-Sanger Cloud Platform (www.i-sanger.com). A Bray-Curtis
218 distance matrix was plotted in a 2-dimensional NMDS ordination, where distance
219 between samples represents their dissimilarity. Sequences were deposited in the NCBI
220 Short Read Archive under Bioproject accession number PRJNA508877, with
221 biosample numbers SAMN10532262–SAMN10532264 (for 16S rRNA genes) and
222 SAMN10532265–SAMN10532267 (for 18S rRNA genes).

223 *2.6. Desalination setup using NF or RO*

224 Bench-scale tests using NF or RO membranes were carried out to verify the positive
225 influence of GDM pretreatment on the subsequent desalination performance. NF and
226 RO membranes were chosen because they were appropriate desalination strategies for
227 the FPW in Sichuan Basin shale gas operation [33,34] due to its low TDS concentration.
228 The permeate stream from the GDM systems was batch-fed to a NF or RO unit. As a
229 comparison, the permeate stream from a traditional UF process was also used as feed
230 water of the desalination processes. Similar to the hollow fiber UF membrane in GDM
231 (Section 2.2), a hollow fiber membrane module (with effective area of 10 cm²) was
232 employed for the traditional UF process. Both GDM filtration and traditional UF
233 process were fed with the same raw shale gas FPW, but the traditional UF process was
234 operated under constant flux mode (with a flux of 50 LMH), as described in a previous
235 study [33]. The NF and RO composite membranes had an active layer of aromatic
236 polyamide and were provided by Vontron Membrane Technology Co., Ltd. (Guiyang,

237 China). The effective filtration area of NF or RO membrane was 14.6 cm^2 . The NF/RO
238 setup is also illustrated in [Fig. S1 \(Supporting Information\)](#), with membrane properties
239 described in detail in previous studies [33,34]. The NF or RO test was performed using
240 a dead-end stirred cell (HP 4750, Sterlitech Corp., Kent, USA) at a stirring speed of 200
241 r/min. Each NF membrane was operated at an applied pressure of 2.0 MPa (20 bar),
242 and it was terminated when a water recovery of 70% was obtained. The RO test was
243 carried out at an applied pressure of 5.0 MPa (50 bar) with a final water recovery of
244 50%.

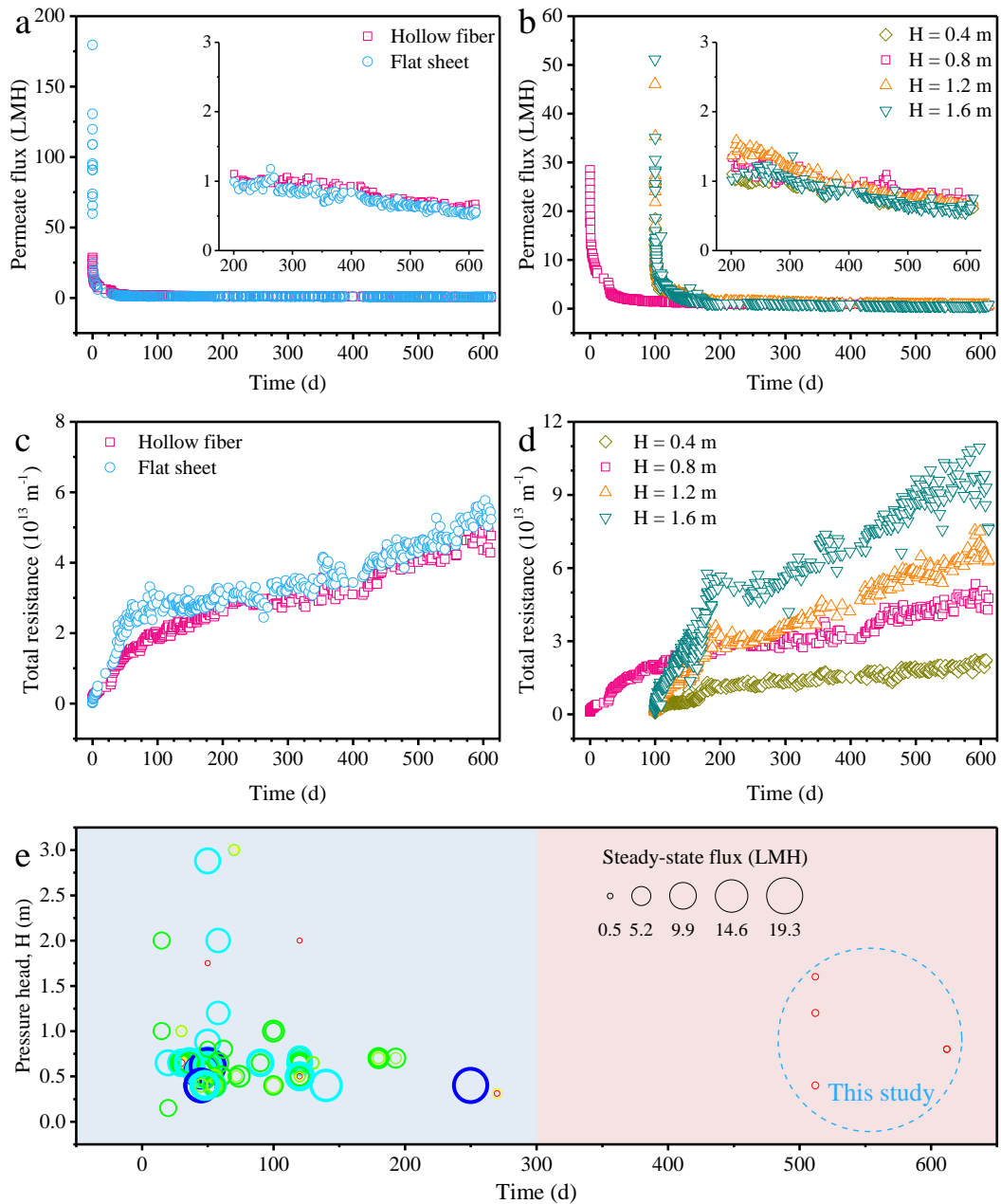
245

246 **3. Results and discussion**

247 *3.1. Behavior of the permeate flux*

248 [Fig. 1](#) illustrates the trend of the permeate flux (normalized to $20 \text{ }^\circ\text{C}$) and the fouling
249 resistance of UF membranes in the GDM systems. As presented in [Fig. 1a](#), the permeate
250 flux using flat sheet membrane declined rapidly due to biofouling from 179 to 8.5 LMH
251 during the first week. After this period, the flux decreased very slowly, reaching a near
252 steady-state flux value of 0.65 ± 0.08 LMH after roughly 300 days of operation. The flux
253 of the hollow fiber UF membranes under the same pressure head of $H = 0.8 \text{ m}$ was
254 initially lower than that observed with flat sheet membranes, consistent with a lower
255 water permeance, but it was also characterized by a rapid decline during the first few
256 weeks of operation, reaching values of 3.0 and 2.0 LMH after 5 and 8 weeks,
257 respectively. The near steady-state value was 0.71 ± 0.10 LMH, observed near the end
258 of the experiment. Therefore, in this study the steady-state flux was not significantly

259 influenced by membrane configuration, orientation, or intrinsic water permeability
 260 coefficient ($p > 0.05$). Flux differences due to the membrane configuration were
 261 reported in previous studies [14-17].
 262



263
 264 **Fig. 1.** Permeate flux and filtration resistance behavior. Variation of (a)(b) normalized
 265 permeate flux and (c)(d) filtration resistance of GDMs during long-term operation: (a)(c)
 266 pressure head, $H = 0.8$ m, and (b)(d) different hydrostatic pressures for hollow fiber

267 membranes; (e) comparison of the steady-state flux of GDMs in this study and in
268 published literature. Detailed information about the steady-state fluxes of GDM
269 systems in published literature are summarized in Table S1 of the Supporting
270 Information.

271

272 The same flux decline and stabilization trend was observed for hollow fiber
273 membranes under different pressure heads (Fig. 1b). The steady-state values (usually
274 reached after roughly one year of operation) were 0.82 ± 0.10 , 0.75 ± 0.09 , and 0.69 ± 0.09
275 LMH for GDMs under pressure heads, H, of 0.4, 1.2 and 1.6 m, respectively. Therefore,
276 the influence of hydrostatic pressure (i.e., height) on steady-state flux values was also
277 not significant, consistent with trends previously reported for the GDM filtration of rain
278 or river water [17,45]. However, the steady-state flux values presented here were lower
279 than those reported by several previous investigations, as summarized in Fig. 1e. This
280 difference is rationalized with the larger pollutant concentrations (e.g., salinity and
281 organics) of the shale gas FPW investigated in this study and with an overall longer
282 operation time (Fig. 1e and Table S1), suggesting that GDM systems should be run for
283 long periods to observe a complete flux behavior.

284 Published studies involving GDM filtration revealed that the predation of eukaryotic
285 microorganisms resulted in the formation of a heterogeneous structure in the biofouling
286 layer, responsible for the observed rapid decline and long-term stabilization of the
287 permeate flux [12,46]. The fouling behavior can also be described in terms of hydraulic
288 resistance. The sharp decrease in the permeate flux of the flat sheet membrane system

289 in the first days of operation led to higher hydraulic resistances compared to hollow
290 fiber membranes in this initial period, but similar resistances were achieved at larger
291 time values (Fig. 1c). As shown in Fig. 1d, the GDM at a pressure head of 0.4 m resulted
292 in the lowest resistance among the systems operated with different pressure heads, with
293 a value of $2.1 \times 10^{13} \text{ m}^{-1}$ at the end of the test. This value was comparable to that
294 observed during GDM filtration of grey water after 120 days [42,47]. Because the
295 observed steady-state fluxes were comparable for the different pressure heads (Fig. 1b),
296 based on Eq. (3) higher hydraulic resistances were associated with increased hydrostatic
297 pressures (Fig. 1d).

298

299 *3.2. Membrane fouling reversibility during GDM filtration*

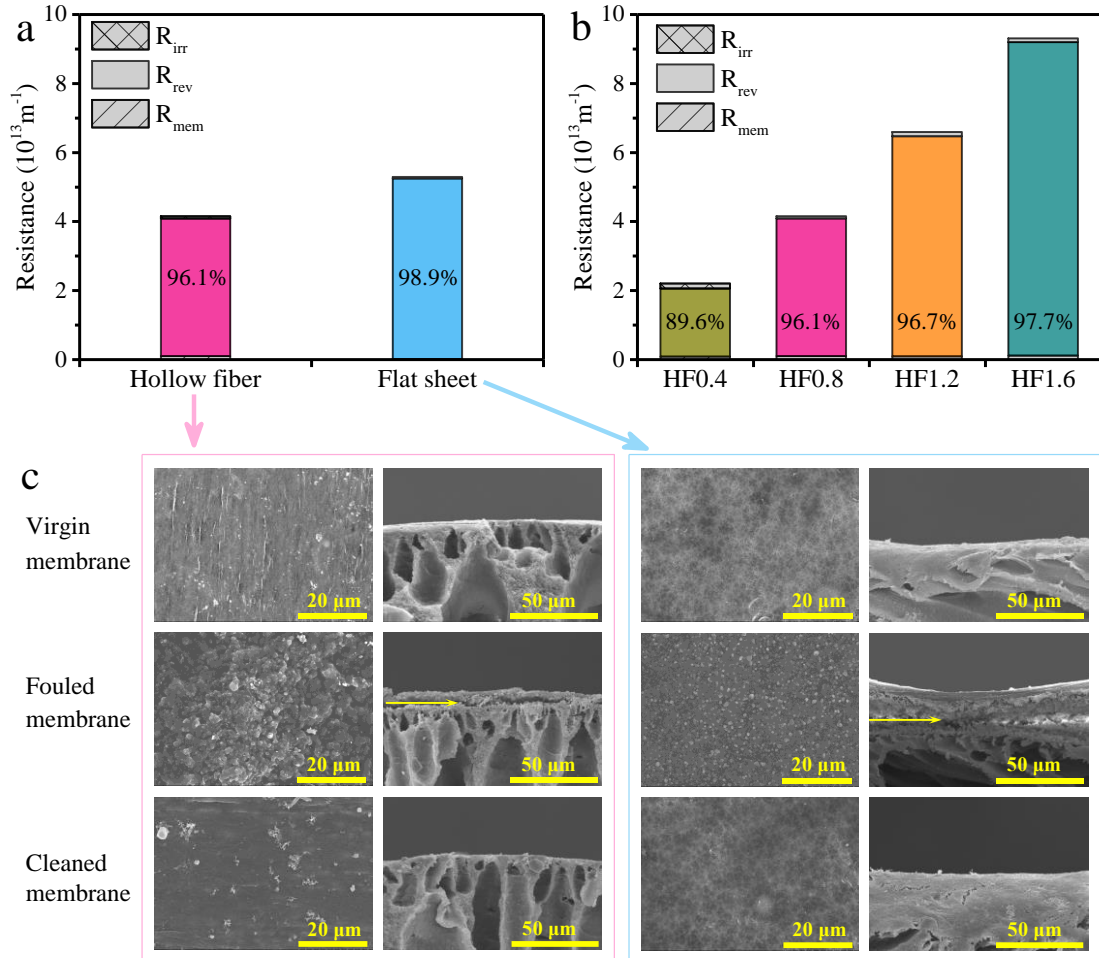
300 Fig. 2 summarizes the results on fouling reversibility of GDMs in shale gas FPW
301 treatment. Regarding membrane configuration (Fig. 2a), near complete recovery of the
302 baseline resistances were observed via hydraulic cleaning for both hollow fiber and flat
303 sheet membranes (96.1% and 98.9%). Moreover, regardless of the value of the pressure
304 head, the dominant reason for flux decline was always the hydraulically reversible
305 resistance, which accounted for a large proportion of the total hydraulic resistance
306 (89.6-97.7%), with increased proportion as the hydrostatic pressures increased (Fig. 2b).
307 These values are consistent with the GDM filtration of grey water, sewage or rain water,
308 reported previously [18,42,47-49]. The results suggest the possibility to effectively
309 recover the flux of GDMs by simple physical cleaning after long-term operation.

310 The GDMs in the two configurations and employed under the same pressure head

311 (0.8 m) were analyzed using SEM after the filtration (612 days) and cleaning steps.
312 While large amounts of deposited foulants was observed on the surface of the
313 membranes following filtration ([Fig. 2c](#)), their efficient removal after physical flushing
314 was confirmed by the micrographs. The thickness of the fouling layer on the flat-sheet
315 membrane (~5.5 μm) was higher than that on the hollow fiber membrane (~4.1 μm),
316 probably due to the different **orientation** (horizontal versus vertical). Note that these
317 thicknesses were tested in this study after membrane drying, which may have led to
318 shrinkage. This is possibly the reason why the thicknesses reported in this study were
319 smaller than those observed previously after GDM filtration of surface water
320 [[11,12,19,20,38,46](#)], grey water [[42,47](#)], rain water [[49](#)], or seawater [[13-15](#)], while they
321 were similar with that obtained after drying the membranes used for the GDM filtration
322 of sewage [[48](#)].

323 The surface contact angle of water may also be used as a proxy to evaluate the fouling
324 reversibility and these results are presented in [Fig. S4](#) of the [Supporting Information](#).
325 The wettability of the hollow fiber membranes increased significantly after filtration
326 (the contact angle decreased), likely due to the deposition of hydrophilic organic
327 foulants [[50](#)]. Following cleaning, the contact angles increased slightly but did not reach
328 the value measured with pristine samples, suggesting that while most of the cake layer
329 was removed, some irreversibly deposited substances were still present on the
330 membrane surface, which did not affect significantly the permeate flux.

331



332

333 **Fig. 2.** Fouling reversibility of the UF membranes. Filtration resistances (a)(b) in
 334 different GDM systems; surface and cross-sectional SEM micrographs (c) of the virgin,
 335 fouled, and cleaned membrane samples. The abbreviations, HF0.4, HF0.8, HF1.2 and
 336 HF1.6, refer to hollow fiber membranes operated under a **pressure head** of 0.4, 0.8, 1.2
 337 and 1.6 m, respectively.

338

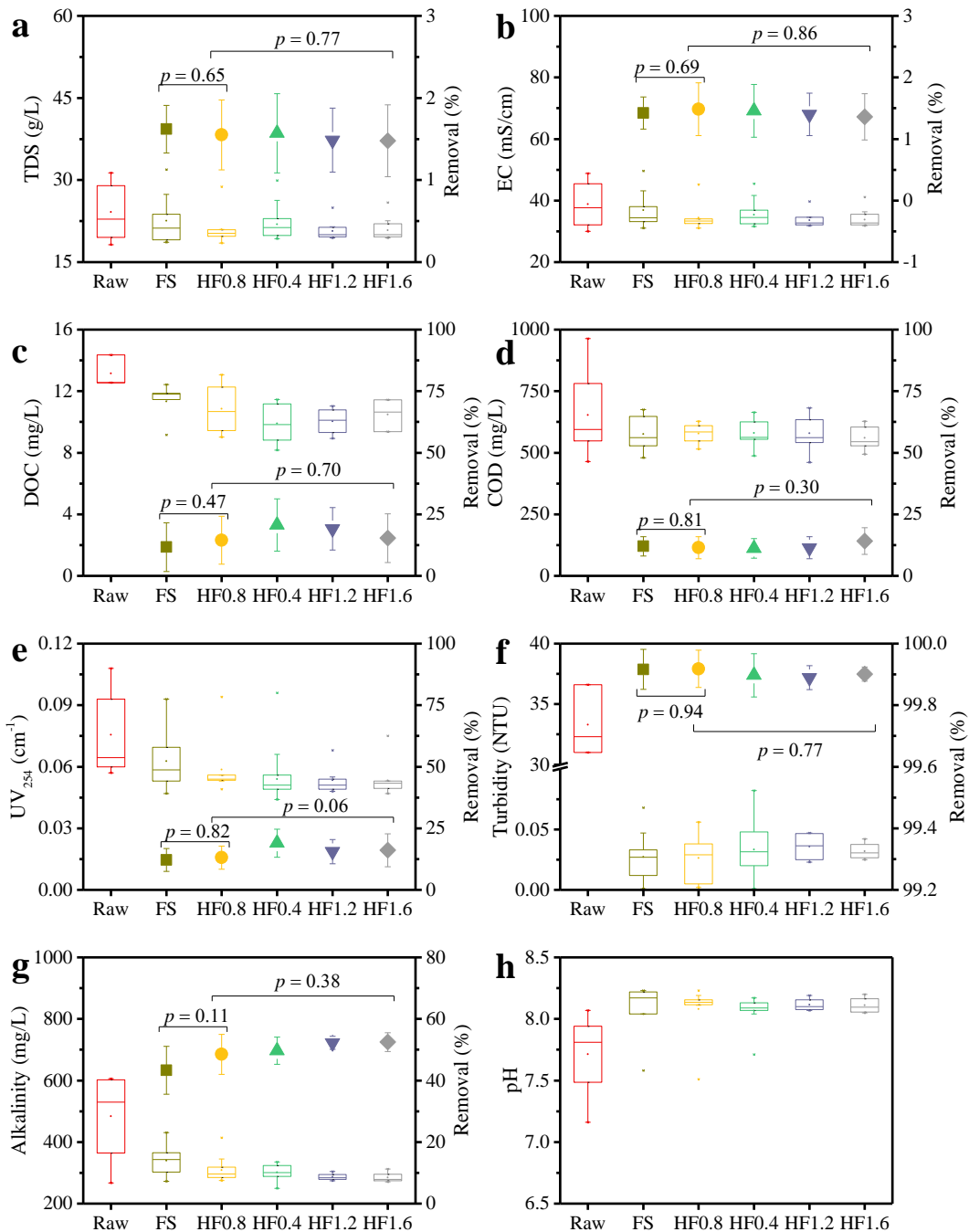
339 3.3. Pollutant removal of GDM from shale gas FPW

340 **Fig. 3** illustrates the permeate quality and the removals of primary pollutants in GDM
 341 systems under different operational conditions. As expected, comparable
 342 concentrations of TDS or EC were observed for the feed water (raw FPW) and the

343 permeates for all the GDM systems (Figs. 3a-b), as these compounds are not effectively
344 removed by UF membranes [33,34]. As shown in Fig. 3c, decreased DOC
345 concentrations were observed in GDM permeates when compared to the raw FPW, with
346 removals in the range 11.7-20.6%. The membrane configuration or hydrostatic pressure
347 did not significantly ($p > 0.05$) influence the DOC removal efficiencies. Similar results
348 were observed for other organic parameters, and the average removals were 11.1-14.2%
349 and 12.2-19.0% for COD and UV₂₅₄, respectively (Figs. 3d-e). The removal efficiencies
350 were similar to those reported for the traditional UF filtration of shale gas FPW
351 [8,33,34].

352 The GDM systems removed instead most of the particulate matter, with residual
353 turbidities lower than 0.05 NTU for the permeates of all the GDMs. The turbidity
354 removals were nearly complete (> 99.9%), as presented in Fig. 3f. With respect to
355 alkalinity, the values in the GDM permeate samples ranged from 249 to 431 mg/L, with
356 removals of 43.3-52.5%. The average pH of the feed water was 7.7, and slightly
357 increased pH values (8.0-8.1) were observe for the permeate streams of GDM systems
358 (Fig. 3h). The results presented here are noteworthy in that they suggest the suitability
359 of GDMs for field application, thus eliminating the need for cumbersome procedures
360 associated with traditional UF processes, such as cross-flow operation, backwashing,
361 and chemical cleaning [10].

362



363

364 **Fig. 3.** Water quality and removal efficiencies of main pollutants in GDM systems.

365 Values of (a) TDS, (b) EC, (c) DOC, (d) COD, (e) UV₂₅₄, (f) turbidity, (g) alkalinity

366 and (h) pH. The box bars represent the concentrations in the raw feed and in the

367 permeate waters, while the solid points represent the corresponding removals. The

368 abbreviation FS refers to flat sheet membranes, while the other abbreviations are the

369 same as in Fig. 2.

370

371 The membrane performance may be deteriorated after exposure to shale gas FPW for
372 a long period [51]. The effects of exposure time (0, 32, 640 d) on membrane
373 performance, including tensile strength, elongation, membrane permeability, and
374 contact angle, are presented in Fig. S5 (Supporting Information). Tensile strength and
375 ultimate elongation decreased for the UF membrane exposed for 32 days when
376 compared to the pristine one, whereas the exposure duration (32 and 640 days) did not
377 have a significant effect on these mechanical properties (Figs. S5a-b). There was no
378 significant difference between the permeability and water contact angle of the pristine
379 UF membrane and that of the membrane exposed for one month, but an obvious
380 decrease in both parameters was observed for the membrane exposed for 640 days (Figs.
381 S5c-d). These results are consistent with SEM observations, which revealed that no
382 obvious foulants were deposited on the membrane surface after exposure for 32 days,
383 while a 640-day exposure promoted large foulant coverage (Fig. S5e). In summary,
384 while the membrane mechanical properties appeared to be more sensitive than other
385 parameters to FPW exposure, their change did not lead to a deterioration of membrane
386 filtration performance or water quality in long-term operation (Fig. 3).

387

388 *3.4. Bacterial and eukaryotic community composition*

389 The bacterial community in the raw FPW consisted of 90 OTUs (Table 1), while the
390 observed OTUs numbers for eukaryotic community ranged between 9 and 32.
391 Compared to the raw shale gas FPW, the observed richness (ACE, Chao) of bacterial

392 community generally decreased in the biofouling layer of GDMs, while that of
 393 eukaryotic community increased. For bacterial community, the decrease in Shannon
 394 and increase in Simpson indices suggest that there was a slight decrease in diversity in
 395 the biofouling layer of GDMs. In contrast, for the eukaryotic community, a higher
 396 diversity of the biofouling layer compared to the raw shale gas FPW was evidenced by
 397 the increase in Shannon index and decrease in Simpson index. The estimates of
 398 community coverage obtained in this study (99.9%) suggest that the presented
 399 sequences represented the vast majority of the microbial community. The rarefaction
 400 curves (Fig. S6, Supporting Information) indicate that most of the bacteria and
 401 eukaryotes reached saturation.

402

403 **Table 1** Abundance, coverage, richness, and diversity of bacterial 16S rRNA genes and
 404 eukaryotic 18S rRNA genes

Sample	No. of sequences	OUT at 97% identity	Coverage	AC E	Chao	Shannon	Simpson
<i>16S rRNA</i>							
FPW	55978	90	1.0000	90.0	90.0	2.86	0.15
HF membrane	48065	82	0.9998	86.6	91.3	2.24	0.21
FS membrane	36997	74	0.9998	80.7	78.7	2.09	0.26
<i>18S rRNA</i>							
FPW	37140	9	0.9999	30.0	12	0.01	1.00
HF membrane	34459	17	1.0000	17.7	17	0.37	0.87
FS membrane	37192	32	1.0000	32.0	32	0.74	0.73

405

406 *3.4.1. Bacterial community of the biofouling layer in GDM and comparison with the*
 407 *raw FPW*

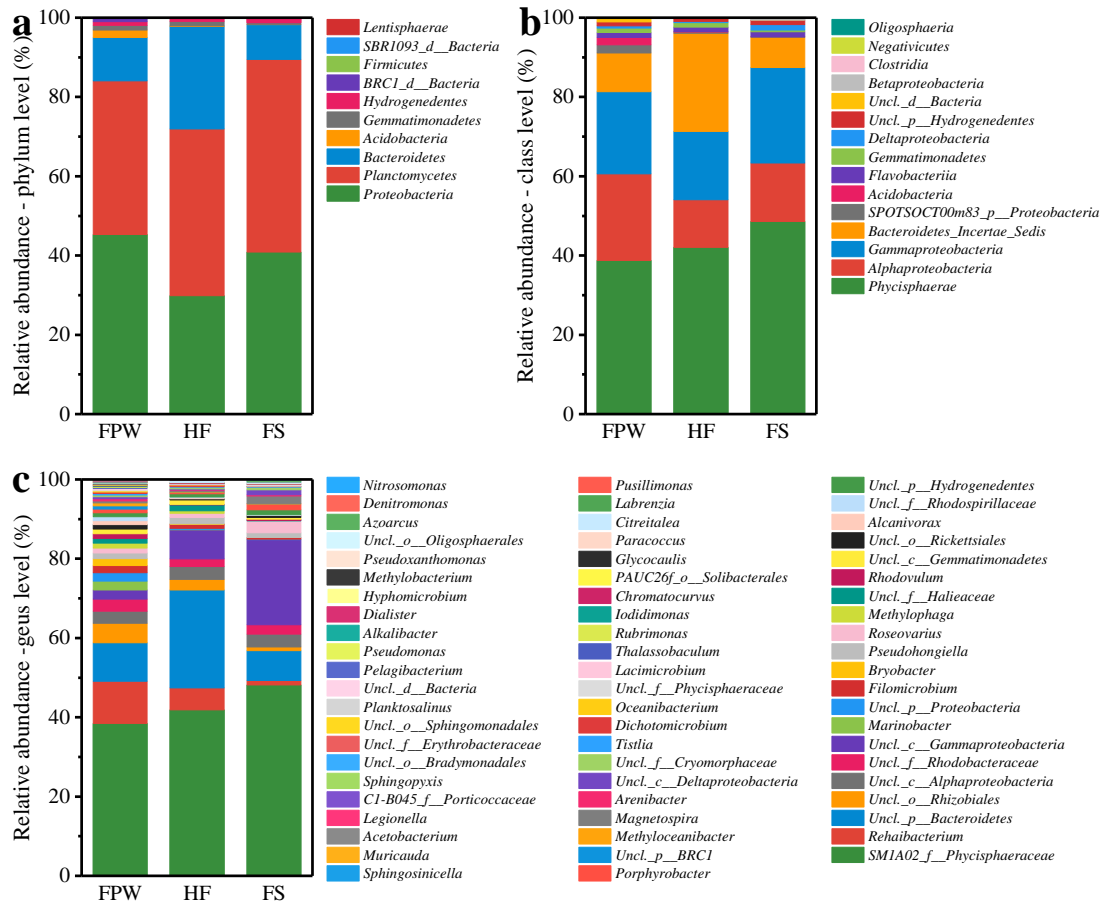
408 Fig. 4 presents taxonomic compositions of bacterial communities. Ten bacterial

409 phyla were detected in the raw shale gas FPW (Fig. 4a), accounting for half of that
410 recovered from shale gas produced water in Sichuan Basin [29]. *Proteobacteria*
411 (45.3%), *Planctomycetes* (38.8%) and *Bacteroidetes* (11.0%) constituted 95% of the
412 bacteria in the raw shale gas FPW. Among these phyla, mesophiles and moderate
413 halophiles [27], i.e., *Bacteroidetes* and *Proteobacteria*, were detected. Bacterial phyla,
414 including *Proteobacteria*, *Planctomycetes*, *Bacteroidetes*, *Acidobacteria*, *Firmicutes*
415 and *Lentisphaerae* [23,26,29,44,52], were also detected in other shale gas FPWs. The
416 dominant classes in shale gas FPW in this study included *Phycisphaerae* (38.8%),
417 *Alphaproteobacteria* (21.9%), *Gammaproteobacteria* (20.7%), and
418 *Bacteroidetes_Incertae_Sedis* (9.8%) (Fig. 4b). The same classes were detected with
419 high abundances in biofouling layers during GDM filtration of seawater [13,16], and
420 comparable microbial diversity was also reported in samples from other shale gas FPWs
421 [26,27,53-56]. At the genus level (Fig. 4c), more than 60 bacteria were recovered in the
422 raw shale gas FPW. Among them, *SMIA02* and *Rehaibacterium* represented each
423 approximately half of the total genera. Most of the genera, such as *SMIA02* and
424 *Rehaibacterium*, *Filomicrobium*, *Bryobacter*, *Roseovarius*, *Methylophaga* and
425 *Alcanivorax* in the shale gas FPW in this work, differed from those detected in Sichuan
426 Basin shale gas produced water [29]. Nevertheless, the genera *Marinobacterium* and
427 *Pseudomonas* have been also reported in previous studies [24,28,30]. As a matter of
428 fact, there is a significant discrepancy between the relative abundance of bacteria (e.g.,
429 in terms of order or gene) in shale gas FPWs reported in the published literature [24,25].
430 This result is most likely due to the significant differences of geographic location, depth,

431 composition of fracturing fluid, well age, and general water quality in this study
432 compared to the previous studies [57].

433 An obvious divergence from raw FPW was observed in terms of dominant bacterial
434 phyla in the GDM biofouling layer (Fig. 4a). For both the hollow fiber and the flat sheet
435 membranes, the relative abundances of *Planctomycetes* and *Proteobacteria* decreased;
436 however, while *Bacteroidetes* increased to 25.9% for the hollow fiber membranes, they
437 decreased to 8.8% in the biofouling layer on flat sheet membranes. At the genera level
438 (Fig. 4c), the proportion of *SM1A02* and *Gammaproteobacteria* increased in the
439 biofouling layers compared to the raw FPW. Some differences of microbial community
440 compositions between the two membrane configurations were observed. *Order_III*
441 (*Bacteroidetes*) became a major microbe in the biofouling layer of hollow fiber
442 membranes, while the relative abundance of both *Rehaibacterium* and *OCS116_clade*
443 (*Rhizobiales*) decreased for flat sheet membranes. Overall, the NMDS plots of Bray-
444 Curtis distances (Fig. S7, Supporting Information) indicated lower dissimilarity of
445 bacterial community between the raw FPW and the biofouling layer of gravity-driven
446 hollow fiber membranes than that between FPW and the biofouling layer of flat sheet
447 membranes.

448



449

450 **Fig. 4.** Bacterial community compositions. Comparison of the bacterial communities in
 451 the raw FPW and in the biofouling layers of hollow fiber and flat sheet GDMs classified
 452 at (a) the phylum level, (b) the class level and (c) the genus level. FPW, HF and FS are
 453 abbreviations for raw shale gas FPW, **GDM filtration using** hollow fiber membrane,
 454 and **GDM filtration using** flat sheet membrane, respectively.

455

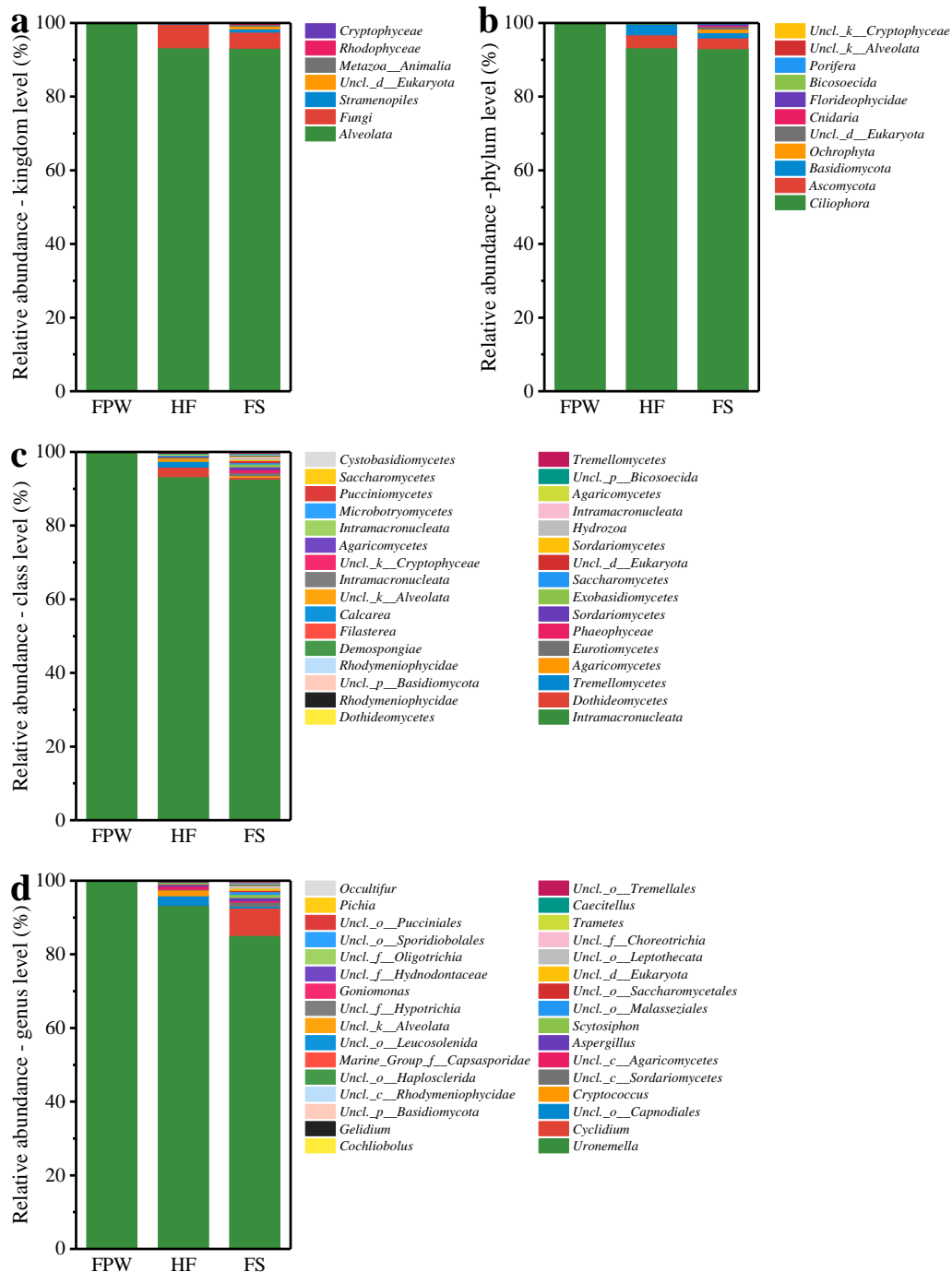
456 *3.4.2. Eukaryotic community of the biofouling layer in GDM and comparison with the*
 457 *raw FPW*

458 As presented in Fig. 5, the vastly predominant eukaryotic phyla in the raw shale gas
 459 FPW were *Ciliophora* (99.46%) in the kingdom of *Alveolata*. At the genus level,
 460 *Uronemella* in the class of *Intramacronucleata* represented the near totality of

461 eukaryotes in the raw FPW. As listed in [Table 1](#), both higher richness and diversity of
462 eukaryotes were observed in the biofouling layer of GDMs compared to the raw shale
463 gas FPW, especially for the flat sheet membranes. This result is evidenced by the
464 increased number of classes or genera, from 8 in the raw shale gas FPW to 15 and 29
465 in GDM biofouling layer using hollow fiber membranes and flat sheet membranes,
466 respectively ([Figs. 5c-d](#)). The Bray-Curtis distances ([Fig. S7, Supporting Information](#))
467 revealed lower dissimilarity between the raw FPW and biofouling layer in hollow fiber
468 GDMs (0.10) than that between raw FPW and biofouling layer in flat sheet GDMs
469 (0.16), and these values were much lower than those observed for the bacterial
470 community (0.27-0.37).

471 More specifically, the relative abundance of fungi increased significantly in the
472 biofouling layer for both membrane configurations. Additionally, other eukaryotic
473 phyla, including *Ochrophyta*, unclassified *Eukaryota*, *Cnidaria*, *Florideophycidae*,
474 *Porifera*, unclassified *Alveolata* (kingdom), and unclassified *Cryptophyceae* (kingdom),
475 were found in the biofouling layer of gravity-driven flat sheet membranes ([Fig. 5b](#)).
476 Most of these fungal communities were also previously reported in shale gas produced
477 water from Sichuan Basin [[29](#)]. However, the kingdoms *Alveolata* and *Stramenopiles*
478 were detected for the first time in shale gas FPW in this study. *Metazoa* were also
479 detected on flat sheet membranes ([Fig. 5](#)). The high abundance of these latter organisms
480 was previously reported in the GDM filtration of surface water and seawater [[12,16,46](#)].
481 The predation by eukaryotic microorganisms is a key factor influencing the biofouling
482 layer structure of GDMs, resulting in a heterogeneous structure and thus a higher

483 steady-state flux than that observed without eukaryotic predation, as discussed in the
 484 literature [12,46].



485
 486 **Fig. 5.** Eukaryotic community compositions. Comparison of the Eukaryotic
 487 communities in the raw FPW and in the biofouling layers of hollow fiber and flat sheet
 488 GDMs classified at (a) the kingdom level, (b) the phylum level, (c) the class level and

489 (d) the genus level. The abbreviations FPW, HF and FS are the same as in Fig. 4.

490

491 *3.5. Evaluation of GDM filtration performance for shale gas FPW treatment*

492 *3.5.1. Effect of GDM on desalination performance of NF and RO membranes*

493 The SDI₁₅ value of the permeate stream from traditional UF was 2.6±0.5, similar to
494 that measured downstream of GDM filtrations. No significant difference was detected
495 in the SDI₁₅ of the permeates from GDMs operated at different pressure heads ($p >$
496 0.05), while a slightly higher SDI₁₅ value was observed downstream of flat sheet
497 gravity-driven membranes compared to hollow fiber membranes. In all the cases, the
498 SDI₁₅ was lower than 3.0, thus appropriate for an effective RO/NF desalination.
499 Moreover, the consistency of flux decline behavior (Fig. 1) with the flow rate of shale
500 gas FPW [3,4,7], further confirmed the sweet spot of GDM for this wastewater
501 treatment.

502 To evaluate the potential of GDM filtration as a pretreatment for FPW desalination,
503 the performance of NF/RO was evaluated using feed solutions from this system or from
504 traditional UF (Fig. 6). Specifically, the mixture of the permeates obtained during the
505 first year of operation of GDM using hollow fiber membranes under different pressure
506 heads ($H = 0.4, 0.8, 1.2$ and 1.6 m) was fed to the NF/RO membranes; this mixed water
507 was used because there was not a significant difference between the primary water
508 parameters (e.g., TDS, EC, DOC, COD, turbidity, alkalinity and SDI₁₅) among these
509 permeates, as presented in Fig. 3 and Fig. 6a.

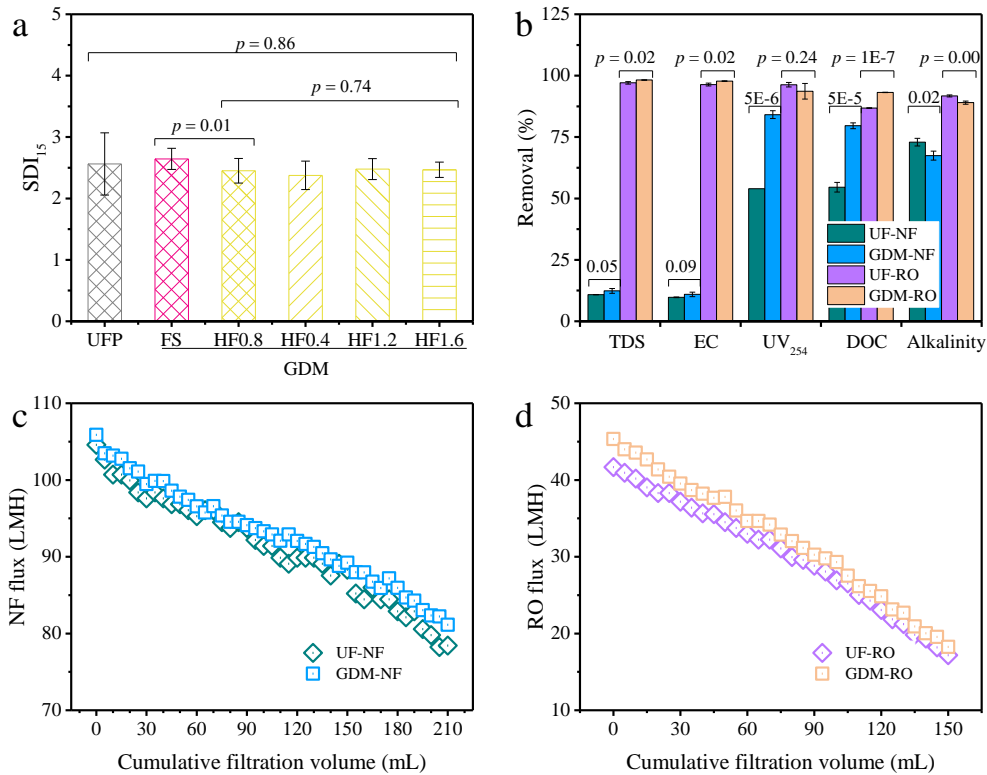
510 During the filtration of FPW, the DOC concentrations of GDM permeate and UF

511 permeate streams were comparable in this study, but the compositions of the DOC may
512 be different. The excitation-emission matrix (EEM) spectra showed that aromatic
513 protein, tyrosine- and protein-like substances were the primary fluorescent substances
514 in raw shale gas FPW [36,58,59]. Additionally, liquid chromatography–organic carbon
515 detection analysis indicated that biopolymers, humic substances, building blocks, low
516 molecular weight (LMW) neutrals or LMW acids composed most of the DOC [58-60].
517 The removal of several organic fractions (e.g., biopolymers and assimilable organic
518 carbon) in the GDM process was significantly higher than that by the traditional UF
519 membrane, whereas more humic acids were rejected by the traditional UF membrane
520 [10]. The different organic compounds resulted in different removals by the subsequent
521 NF or RO units. Similar correlations were obtained in the filtration of seawater [16].
522 The superiority of GDM over traditional UF as NF pretreatment in organic removals is
523 possibly due to the lower concentration of biopolymers assimilable organic carbon in
524 the permeate stream, as demonstrated by Wu et al. [16]. Moreover, the pH values of the
525 GDM permeate (Fig. 3h) were slightly higher than that of the UF permeate (~8.0) [34],
526 and a higher DOC removal during nanofiltration of hydraulic fracturing wastewater
527 with the increase in pH has been reported [61]. Thus, the overall organic removal
528 efficiency (i.e., UV_{254} and DOC) of the NF membrane was improved when the GDM
529 permeate was used as the feed water ($p < 0.05$), as presented in Fig. 6b. Also, the
530 removal of TDS and EC in NF was slightly larger when treating GDM compared to UF
531 permeate. On the other hand, the higher proportion of bicarbonate in the GDM permeate
532 led to a lower removal of alkalinity in the following NF unit. Although a high removal

533 of bicarbonate by NF membrane was reported [62], the removal efficiency of
534 monovalent ion (HCO_3^-) was less than that of divalent ion (CO_3^{2-}). With respect to
535 membrane fouling, the NF fluxes following GDM pretreatment were slightly larger
536 than that after UF pretreatment, with an increase of 1-5%, as shown in Fig. 6c.

537 In RO, higher removal rates of TDS, EC, DOC and alkalinity were observed when
538 using GDM permeate as the feed compared to the traditional UF permeate ($p < 0.05$),
539 while the removal of UV_{254} was comparable ($p > 0.05$). However, a higher RO flux was
540 observed when treating the GDM permeate compared to the traditional UF-RO process
541 (Fig. 6d). This increase (4-10%) is regarded as significant, also considering that the
542 NF/RO unit was run in dead-end mode. The advantage of GDM to traditional UF as
543 RO pretreatment was also reported in seawater desalination for a 10-day operation [16],
544 and attributed to lower concentrations of assimilable organic carbon in the GDM
545 permeate. The permeate flux of RO membranes could be further improved when the
546 GDM permeate stream was treated using a granular activated carbon filter or NF
547 membrane (data not shown), or when the operation mode was optimized (e.g.,
548 crossflow filtration).

549



550

551 **Fig. 6.** Effect of GDM and traditional UF pretreatment on the desalination performance
 552 of NF and RO membranes: (a) SDI₁₅ of the GDM permeate, (b) pollutant removals by
 553 NF/RO membrane treating GDM and traditional UF permeates, (c) flux decline in NF,
 554 and (d) flux decline in RO.

555

556 3.5.2. Application implications and outlook

557 Membrane technologies have potential application for the treatment and reuse of
 558 shale gas FPW [6]. For GDM systems, the permeate flux commonly decreases in the
 559 first several days of operation, before flux stabilization is obtained (Fig. 1). This flux
 560 decline trend is similar to the flowback rate of shale gas FPW (from 1,000 to 2-8 m³/d)
 561 [3,7]. This implicates that the GDM filtration is suitable to also treat shale gas FPW in
 562 field applications. The flux stabilization of GDM systems was independent of

563 membrane configuration or hydrostatic pressure. Thus, the similarities in performance
564 observed for hollow fiber and flat sheet membranes suggest that the former
565 configuration may be advantageous due to its larger specific surface area, thus
566 translating into a smaller overall plant footprint. While the absolute values of steady-
567 state flux are relatively low, they are justified by the nature of the driving force, a
568 pressure head, which requires little external energy input to be maintained during
569 filtration.

570 The pollutant removals of GDM systems (Figs. 3 and 6) showed their suitability for
571 field application, and GDM filtration outperformed the traditional UF as pretreatment
572 for the subsequent NF unit (increase by 1-5%) and RO unit (with an increase of 4-10%)
573 (Fig. 6). As opposed to the cumbersome procedures (e.g., periodic backwashing or
574 chemical cleaning [11]) of traditional UF process, the GDM system is an energy-
575 efficient process due to the nature of the driving force, i.e., gravity. Thus, the energy
576 demand of GDM system is in the order of 0.01 kWh/m³ [10,63], depending on feed
577 water characteristics. This value is significantly lower than the overall energy demand
578 of conventional UF system (~0.3 kWh/m³) [63,64]. On the other hand, the low flux is
579 a potential limitation of GDM system, resulting in a larger footprint or a larger
580 membrane area. For example, the steady-state flux of the GDM under a pressure head
581 of 0.4 m (0.82 LMH) was less than 5% that of a conventional UF system (19 LMH,
582 with a water recovery of 93%) observed during the filtration of shale gas FPW [33].
583 Thus, the membrane costs (investment and replacement) of GDM are higher than in
584 traditional UF to produce the same volume of total permeate. Recently, Pronk et al. [10]

585 compared the total costs of GDM and traditional UF systems based on different scales.
586 The stable flowback rate of shale gas FPW was 2-8 m³/d per well [10]. Overall, the
587 capital expenditure and membrane replacement costs for GDM and traditional UF
588 systems depend very much on the specific conditions and on the size of the plant;
589 however, the GDM system always had lower operational costs than the traditional UF
590 process (i.e., chemical costs, energy costs, operation & maintenance), demonstrating
591 that GDM may be attractive for FPW treatment under several circumstances..

592 Moreover, further studies to optimize the GDM system may address operational
593 optimization, including length and parameters of filtration and washing cycles, with the
594 goal to maintain high fluxes and to decrease membrane investment costs. Importantly,
595 understanding the nature of the biofouling layer is critical for investigations aimed at
596 minimizing fouling and optimizing filtration and cleaning cycles.

597

598 **4 Conclusion**

599 The performance of GDM filtration as pretreatment for the desalination of shale gas
600 FPW was evaluated over a 612-day operation. The following conclusions can be drawn:

601 (1) The flux stabilization of GDM systems was independent of membrane
602 configuration or hydrostatic pressure, and the steady-state values were in the range
603 0.65-0.82 L m⁻²h⁻¹. The resistance associated to reversible fouling accounted for more
604 than 89% of the total hydraulic resistance. While the absolute values of steady-state
605 flux are relatively low, they are justified by the nature of the driving force, a pressure
606 head, which requires little external energy input to be maintained during filtration.

607 (2) There was not a significant difference in the removal of TDS, organics, turbidity
608 and alkalinity for the different GDM systems. The GDM filtration outperformed
609 traditional UF as a desalination pretreatment, **resulting in higher organic removal**
610 **efficiencies and improved flux, especially for the RO system.** While GDM filtration
611 also relies on UF membranes for the aqueous separation, there are several advantages
612 compared to traditional UF, including the absence of backwashing, cross-flow, and
613 chemical cleaning. Overall, this translates into a substantial gain in terms of ease of
614 operation and economic savings.

615 (3) The raw shale gas FPW contained more than 60 bacterial genera, with *SMIA02*
616 and *Rehaibacterium* representing approximately half of the total genera. Eukaryotic
617 communities in the kingdoms of *Alveolata* and *Stramenopiles* were detected for the first
618 time in shale gas FPW.

619 (4) The bacterial community diversity decreased while the eukaryotic community
620 diversity increased in the biofouling layer of GDMs, when compared to those of raw
621 shale gas FPW. The predation by eukaryotic microorganisms including *Alveolata*,
622 *Fungi*, *Stramenopiles* and *Metazoa* played an important role in flux stabilization during
623 GDM filtration. Understanding the nature of the biofouling layer is critical for
624 investigations aimed at minimizing fouling and optimizing filtration and cleaning
625 cycles.

626 (5) For a long-term exposure, the variations of membrane permeability and contact
627 angle were less significant than those related to elongation and tensile strength of the
628 membranes. On the whole, long-term exposure to highly contaminated streams seems

629 to have no significant detrimental effect on system performance.

630

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640

641 **Appendix A. Supplementary data**

642 Supplementary data related to this article can be found online.

643

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