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1 Reuse of shale gas flowback and produced water:
2 effects of coagulation and adsorption on
3 ultrafiltration, reverse osmosis combined process

4 Revised for

5 *Science of the Total Environment*

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18

19

20 **Abstract**

21 The shale gas flowback and produced water (FPW) from hydraulic fracturing in the Sichuan
22 province of China has relatively low to moderate levels of total dissolved solids (< 20 g/L) and
23 organics (< 50 mg/L of dissolved organic carbon). As such, a combined ultrafiltration (UF),
24 reverse osmosis (RO) system can be successfully applied to desalinate this feed water with the
25 goal of reuse. However, the concentration of influent organic matter and particulates in the UF
26 and RO stage is high, and the overall ionic and organics composition is highly complex, so that
27 the membrane processes do not perform well, also due to fouling. To ensure the long-term and
28 efficient operation of the UF-RO stages, a **combined** pretreatment of the FPW with coagulation
29 and adsorption was investigated. The effect of different parameters on the performance on the
30 system was studied in detail. Overall, the coagulation-adsorption pre-treatment greatly reduced
31 fouling of the membrane processes, thanks to the high removal rate of turbidity (98.8%) and
32 dissolved organic carbon (80.4%). The adsorption of organic matter by powdered activated
33 carbon was best described by the Freundlich equilibrium model, with a pseudo second-order
34 model representing the adsorption kinetics. Also, the various ions had competitive removal rates
35 during the adsorption step, a phenomenon reported for the first time for FPW treatment. Also, an
36 optimal dose of activated carbon existed to maximize fouling reduction and effluent quality. The
37 overall treatment system produced a high-quality water streams, suitable for reuse.

38 **Keywords:** Flowback and produced water, Adsorption, Coagulation, Ultrafiltration, Reverse
39 osmosis, Water quality

40

41

42 **1. Introduction**

43 Shale gas has attracted attention in the energy field as an unconventional natural gas resource
44 with potentially low carbon footprint and globally abundant reserves (Butkovskyi et al., 2017;
45 Estrada and Bhamidimarri, 2016; Howarth et al., 2011; Vidic et al., 2013). China has the world's
46 largest shale gas reserves of 25.08 trillion cubic meters. The Sichuan Basin is China's largest
47 storage of shale gas and includes the most productive commercial shale gas field (Zhang et al.,
48 2019; Zou et al., 2018). However, a large amount of **flowback and produced water (FPW)** is
49 produced during the process of mining shale gas, **ranging from 5,200 to more than 25,000 m³ for**
50 **each horizontal well (Chang et al., 2019a; Kondash and Vengosh, 2015; Zou et al., 2018).**

51 The hydraulic fracturing wastewaters are highly variable in their composition, **both spatially and**
52 **temporally (Barbot et al., 2013; Chang et al., 2019a).** The high concentrations of particulates,
53 colloids, hardness, salinity, organic matter, and radioactivity (Luek and Gonsior, 2017; Vengosh
54 et al., 2014; Xiong et al., 2016), **require extensive and non-conventional FPW treatment for its**
55 **possible reuse or direct discharge (Chang et al., 2017). Compared to the FPW typically generated**
56 **in basins in the USA (Chang et al., 2019a), the FPW from Sichuan basin is not only estimated to**
57 **contain a lower level of TDS (6906 – 28,900 mg/L) (Chang et al., 2019a; Chen et al., 2015; Guo**
58 **et al., 2018; Huang et al., 2016), but it is also characterized by a lower amount of organic matter**
59 **(total organic carbon (TOC) is approximately 78 mg/L) (Kong et al., 2017).** There are other
60 important differences for the FPW from different regions, such as the types and mixture of ions,
61 organic matters, and the presence of radioactive materials. **The FPW has** the potential to
62 contaminate groundwater, soil, and air, posing great risks to human and ecosystem health in the
63 case of improper management (Annevelink et al., 2016; Howarth et al., 2011; Shaffer et al.,

64 2013; Stoll et al., 2015). Therefore, for the Sichuan basin, China's shale gas mining areas, and
65 the world at large, it is extremely urgent to create a process to manage a plethora of FPWs
66 having each their own specific characteristics.

67 External reuse is a promising wastewater management approach for shale gas FPW
68 (Butkovskiy et al., 2017; Chang et al., 2019a; Guo et al., 2018; Harkness et al., 2015). China, as
69 well as the rest of the world, still lacks efficient processing technologies and rational systems for
70 reuse of these streams in irrigation or for recycling in additional fracking operations. Reliable
71 research on FPW reclamation is arguably the primary task of shale gas exploration at this stage.
72 Membrane-based processes are certainly promising techniques for FPW recycling due to their
73 high efficiency and excellent permeate quality (Chang et al., 2019a; Estrada and Bhamidimarri,
74 2016; Shaffer et al., 2013), including microfiltration, ultrafiltration, nanofiltration, forward
75 osmosis (FO), reverse osmosis (RO), or their combination. Among them, reverse osmosis is
76 regarded as the most energy-saving and promising water desalination technology (Elimelech and
77 Phillip, 2011). However, membrane fouling is still one of the critical difficulties in the
78 implementation of membrane filtration processes (Chang et al., 2019a). Numerous studies have
79 been conducted to control or reduce membrane fouling, including optimization of operational
80 parameters and application of effective pretreatment (Amin Reyhania, 2015).

81 Coagulation is a relatively simple physical-chemical technique to treat FPW, reducing
82 organics and thus alleviating membrane fouling. Rosenblum et al. confirmed that coagulation
83 could remove 80% of total petroleum hydrocarbons and 90% of turbidity (Rosenblum et al.,
84 2016). In a previous study, 33.6-62.0% and 33.6-42.6% of COD was removed by addition of
85 aluminum sulfate or ferric chloride, respectively, and 64% and 84% of UF fouling was decreased
86 by these coagulants under optimal dosage (Chang et al., 2019b). However, the use of coagulants

87 results in an increase in the concentration of aluminum or iron in the effluent water. Adsorption
88 may be thus applied to further polish this stream before further treatment based on membranes.
89 Activated carbon is an excellent adsorbent which remains widely used, mainly due to its high
90 adsorption capacity, adsorption speed, good mechanical stability (Liu et al., 2012), although the
91 effect of powdered activated carbon (PAC) on membrane fouling is still debated (Shao et al.,
92 2017; Wang et al., 2016). Additionally, the PAC regeneration process and the post-treatment of
93 the adsorbed substances may also increase the operational cost. When treating FPW, PAC
94 achieved greater than 80% reductions of the total ion chromatogram, while dissolved organic
95 carbon (DOC) removals were between 9.5 and 48.3% (Rosenblum et al., 2016). The combined
96 process of coagulation and adsorption can greatly reduce the dissolved organics, turbidity, and
97 ion concentrations (Rosenblum et al., 2016), while also reducing the consumption of activated
98 carbon. However, little research has been performed on such combined process, and specifically
99 on its role to optimize membrane filtration processes in the treatment of FPW.

100 The objective of this study is to evaluate the feasibility of a hybrid coagulation-adsorption-
101 UF-RO system in assisting FPW reuse in Weiyuan shale gas operation. The performance of the
102 system, the influence of coagulation and activated carbon on membrane performance and their
103 effects in the removal of dissolved organics are systematically investigated. The results of this
104 study allow the evaluation of coagulation-adsorption to alleviate membrane fouling and the
105 applicability of this process for the treatment of FPW. Another objective of the study is to
106 provide a better understanding of UF and RO fouling from FPW and discuss solutions that
107 enable the use of membrane filtration in the recycling of wastewater produced during shale gas
108 exploration.

109

110 **2. Materials and methods**

111 **2.1 Shale gas FPW samples**

112 The flowback and produced water sample utilized in this study was collected from a well site of
113 the Weiyuan shale gas field located in the Sichuan province of China. The site includes 6
114 horizontal wells that were hydraulically fractured on a single pad using similar fracturing fluid.
115 Wastewater from previously completed wells and fresh water were mixed and stored in a storage
116 pool. The stock samples were packed at the pool into plastic cylindrical containers and then
117 transported to the lab. Its characteristics are summarized in Table 1. The containers were sealed
118 and stored in a dark place to minimize variation of their characteristics in time.

119

120 **Table 1.** Quality of the influent water and of the effluents from each treatment step of the hybrid
 121 system investigated in this study^a

Constituent	FPW in Weiyuan	Coagulation	PAC ^b Adsorption	UF membrane permeate	RO membrane permeate
Turbidity (NTU)	187	15.8	2.1	0.08	0.07
UV ₂₅₄ (1/cm)	0.137	0.077	0.015	0.016	0.003
TDS (mg/L)	16320	15715	15930	15410	224
Conductivity (mS/cm)	26.79	26.29	26.20	25.85	0.52
DOC (mg/L)	38.03	13.61	5.21	5.19	1.71
SUVA (L mg ⁻¹ m ⁻¹)	0.36	0.46	0.21	0.22	0.17
pH	7.48	6.93	7.31	7.51	6.65
Na ⁺ (mg/L)	6151	6065	5920	5931	105
Ca ²⁺ (mg/L)	274.7	257.9	201.2	200.9	1.1
Mg ²⁺ (mg/L)	36.5	34.8	26.5	26.4	-
K ⁺ (mg/L)	255.1	246.2	175.7	173.3	2.5
Sr ²⁺ (mg/L)	66.3	57.3	28.9	28.4	-
Ba ²⁺ (mg/L)	94.4	90.2	63.9	61.3	-
NH ₄ ⁺ (mg/L)	60.4	60.2	50.1	50.3	1.3
Cl ⁻ (mg/L)	9412	9275	9158	9133	149
NO ₂ ⁻ (mg/L)	35.7	31.0	28.5	28.5	1.3
F ⁻ (mg/L)	12.6	11.5	9.4	9.3	0.2
Br ⁻ (mg/L)	97.9	94.2	89.8	89.8	1.7
NO ₃ ⁻ (mg/L)	161.9	151.9	139.9	138.8	1.2

122 ^a The data in the table is the average of three replicate experimental data.

123 ^b Adsorption experiment at optimal dose of 300 mg/L of WP260.

124

125

126 2.2 Chemicals and materials

127 Aluminum sulfate octadeca hydrate ($\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$; Sigma Aldrich, analytical grade) was
128 used as a coagulant. The reagents for chemical oxygen demand (COD) analysis were purchased
129 from Lianhua Tech Co., Ltd. (Lanzhou, China). Concentrated sulfuric acid was obtained from
130 Kelong Chemical (Chengdu, China). Three types of powdered activated carbon (WP260,
131 PAC70X, DCL320) were purchased from Calgon Carbon Corporation (Moon Township, PA,
132 USA). The detailed characteristics of the activated carbon samples are listed in Table 2. The size
133 distributions of these adsorbents are shown in Fig. S2 of the Supporting Information.

134 **Table 2.** Characteristics of three different activated carbon products investigated in this study

Product name	Specific surface area (m^2/g)	Total pore volume (cm^3/g)	Avg pore diameter (nm)	Moisture wt%	Ash wt%	US mesh (<325) wt%	Iodine No. (mg/g)
WP260	1392	1.05	3.01	6	14	72	1023
PAC70X	882	0.44	1.99	5	15	84	732
DCL320	933	0.54	2.31	7	-	80	-

135

136 A polyvinylidene fluoride (PVDF) hollow fiber membrane (Litree Purifying Technology Co.,
137 Ltd., Haikou, China) was employed for the UF treatment. This membrane (pore size in the range
138 of 11.3-28.8 nm) had a molecular weight cut-off (MWCO) of 100 kDa, and the outside diameter
139 of the fiber was 1.8 mm. In each UF test, a single fiber with a length of 20 cm was used, and the
140 effective surface area was 11.3 cm^2 . The SW21 from Vontron Membrane Technology Co., Ltd.

141 (Guiyang, China) was selected as RO membrane. The effective area of each RO membrane
142 coupon was 14.6 cm².

143 **2.3 Analytical methods**

144 The temperature and pH were measured using a mercury thermometer and a pH meter,
145 respectively (PB-10, Sartorius Scientific Instruments Co., Ltd., Beijing, China). The turbidity
146 was determined with a Hach TL2310 (Hach, Loveland, CO, USA) turbidimeter. An Ultrameter II
147 6PFC (Myron L, Carlsbad, California, USA) portable multi-function instrument was adopted to
148 determine the TDS and conductivity. The fast digestion-spectrophotometric method was utilized
149 to measure the COD using a 5B-1F(V8) fast digestion instrument (Lianhua Environmental
150 Protection Technology Co., Ltd., Lanzhou, China). UV absorbance at 254 nm was measured by
151 UV-Vis spectrophotometry (Orion AquaMate 8000, Thermo Fisher Scientific Inc., MA, USA).
152 The dissolved organic carbon (DOC) content was measured using a TOC analyzer L series
153 (Shimadzu, Kyoto, Japan). SUVA₂₅₄ (L/mg·m), an indicator of aromatic dissolved organic
154 matter, was defined as UV₂₅₄ absorbance divided by DOC concentration. The quantification of
155 the concentrations of Cl⁻, Br⁻, F⁻, NO₂⁻, NO₃⁻, Na⁺, K⁺, NH₄⁺, Ca²⁺, Mg²⁺, Ba²⁺, Sr²⁺ was
156 performed using a Dionex ICS-1100 ion chromatographer (Thermo Fisher Scientific Inc., MA,
157 USA). The techniques of scanning electron microscopy (SEM) and energy dispersive
158 spectroscopy (EDS) (Regulus 8230, HITACHI, Tokyo, Japan) were used to investigate the
159 morphology and elemental ratio of the membrane surface and fouling layers. Before SEM-EDS
160 analysis, the membranes were coated with 2 nm of gold using a magnetron sputter (MSP-2S,
161 IXRF Systems, USA). The Brunauer-Emmett-Teller (BET) specific surface areas and porosity
162 were determined by means of nitrogen-sorption isotherms with a NOVA 2200e analyzer
163 (Quantachrome, USA).

164 **2.4 Experimental procedures**

165 ***2.4.1 Treatment protocols***

166 The overall design of the proposed system (Fig. S1) is as follows: coagulation, activated carbon
167 adsorption, ultrafiltration, and finally reverse osmosis. Unless otherwise specified, the
168 operational temperature was 293 ± 1 K for all the experiments. In the jar coagulation tests,
169 aluminum sulfate was chosen as flocculant and the optimum dose was 600 mg/L according to
170 our previous work.(Chang et al., 2019b) Experiments were conducted with the ZR4-6 jar-test
171 equipment (Zhongrun Water Industry Technology Development Co., Ltd., Shenzhen, China).
172 After adding the coagulant to a raw water sample, the experimental procedure consisted of two
173 subsequent stages: a rapid mixing stage at 200 rpm for 1 min followed by slow mixing at 40 rpm
174 for 20 min. The stirring was then stopped, and the mixture was allowed to settle for 30 min.
175 Finally, the supernatant was removed from the beaker for analysis and subsequent experiments.
176 For adsorption experiments, the three types of PAC were rinsed with ultrapure water to remove
177 undesired surface compounds and dried at 377 K for 24 h. The raw water or the samples obtained
178 from coagulation tests were treated by adsorption with the addition of PAC in the jar-test
179 equipment mentioned above, while stirring at 80 rpm for different time intervals in the range 15-
180 120 min. A series of PAC dosages (50, 150, 300, 800, and 1200 mg/L) were tested.

181 New UF and RO membranes were soaked in ultrapure water for at least 48 h and the water
182 was replaced at least three times. A new membrane was used for each UF run and a filtration
183 with ultrapure water for 1 h was performed to obtain a stable water flux. Then, multi-cycle UF
184 tests with periodic hydraulic backwash were executed at a constant flux equal to $50 \text{ L m}^{-2}\text{h}^{-1}$
185 (LMH). The duration of each filtration and backwash step was 54 min and 3.5 min, respectively,
186 for each cycle. The transmembrane pressure (TMP) was measured using a pressure sensor (Unik

187 5000, General Electric Company, USA) in constant flux mode, which was controlled
188 continuously with a pressure gauge (1379 Duragauge, Ashcroft Inc., USA) connected to the
189 peristaltic pump. The permeate solution tank rested on an electronic balance (Adventurer Pro
190 CAV8101, Shanghai, China) and weight changes were recorded over time to determine the
191 permeate flux.

192 The RO unit was operated using a dead-end stirred cell (HP 4750, Sterlitech Corp., Kent,
193 WA, USA). These tests were carried out at the constant transmembrane pressure of 5.5 MPa (55
194 bar). The solution in the filtration cell was kept under stirring at 200 rpm. The initial feed volume
195 in the RO cell was 300 mL and the filtration was continued until a recovery rate of 50% was
196 achieved (150 mL of permeate solution was collected).

197 **2.4.2 Analyses and calculations**

198 Following adsorption, the DOC content of the supernatant solution was measured. The uptake of
199 adsorbate by PAC, q_e (mg DOC/g), was calculated according to the following
200 equation(Sontheimer et al., 1988):

$$201 \quad q_e = \frac{V(C_0 - C_e)}{m} \quad (1)$$

202 where q_e is the equilibrium adsorbent-phase concentration of adsorbate (mg adsorbate/g
203 adsorbent), C_0 and C_e are the initial and equilibrium liquid phase concentrations of the organic
204 adsorbates (mg DOC/L), respectively, V is volume of the solution (L), and m is the weight of the
205 PAC (g) adsorbent. Freundlich, Langmuir, and Temkin isotherm models were assessed to
206 describe the mechanism of phase partitioning. The Freundlich isotherm model can be expressed
207 by Eq. (2):(Cheng et al., 2015)

208
$$q_e = K_F C_e^{\frac{1}{n}} \quad (2)$$

209 Eq. (2) can also be expressed in the linearized logarithmic form:

210
$$\log(q_e) = \log(K_F) + \frac{1}{n} \log(C_e) \quad (3)$$

211 where K_F is the Freundlich adsorption capacity parameter, and $1/n$ is the dimensionless
212 Freundlich adsorption intensity parameter. The intercept and slope of the line in equation 3
213 enable the determination of the isotherm constants. Langmuir isotherm model is expressed
214 as:(Manz et al., 2016)

215
$$q_e = \frac{Q_M K_L C_e}{1 + K_L C_e} \quad (4)$$

216 The linear equation of Eq. (4) is expressed as:

217
$$\frac{C_e}{q_e} = \frac{C_e}{Q_M} + \frac{1}{K_L Q_M} \quad (5)$$

218 where K_L is the Langmuir adsorption constant, and Q_M is the maximum adsorbent phase when
219 the adsorbent is saturated. The Temkin isotherm model contains a factor that explicitly takes into
220 account the adsorbate-adsorbent interactions. This model assumes the following: (i) the heat of
221 adsorption of all the molecules in the layer decreases linearly with coverage due to adsorbent-
222 adsorbate interactions, and (ii) the adsorption is characterized by a uniform distribution of
223 binding energies, up to a maximum binding energy(Angin, 2014). The Temkin isotherm model is
224 presented in the following form:

225
$$q_e = B \ln(K_T \cdot C_e) \quad (6)$$

226 Eq. (6) can be written in the linear form:

$$227 \quad q_e = B \ln(K_T) + B \ln(C_e) \quad (7)$$

228 where B is the Temkin constant related to gas constant, heat of sorption, and absolute
229 temperature, K_T is the equilibrium binding constant (L/mg). The adsorption coefficients can be
230 computed by plotting q_e values vs. $\ln C_e$.

231 In order to describe the speed of the adsorption process, pseudo first-order and pseudo second-
232 order kinetic models were selected to assess the experimental data. The models were expressed
233 with the following equations:(Cheng et al., 2015)

$$234 \quad \log(q_e - q_t) = \log q_e - \frac{k_1 t}{2.303} \quad (8)$$

$$235 \quad \frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e} \quad (9)$$

236 where q_e and q_t (mg/g) are the adsorbent capacities at equilibrium and at time t (h), respectively;
237 k_1 (h^{-1}) and k_2 ($\text{g}/(\text{mg}\cdot\text{h})$) are the pseudo first-order and pseudo second-order rate constants,
238 respectively.

239 The total fouling index (TFI) was used to quantify the UF membrane fouling of different
240 operational cycles and cleaning steps (Chang et al., 2016; Nguyen et al., 2011). **The derivation**
241 **process for the TFI parameter is provided in the SI. And** the TFI was calculated by equation (10):

$$242 \quad (TFI)V_s = \frac{TMP_f}{TMP_0} - 1 \quad (10)$$

243 where V_s (L/m²) is the volume of filtered water per unit membrane area; the TMP at the
244 beginning and end of the filtration is represented by TMP₀ and TMP_f (kPa), respectively. This
245 index was calculated by the least square linear regression approach.

246 **3. Results and discussion**

247 **3.1 Adsorption processes**

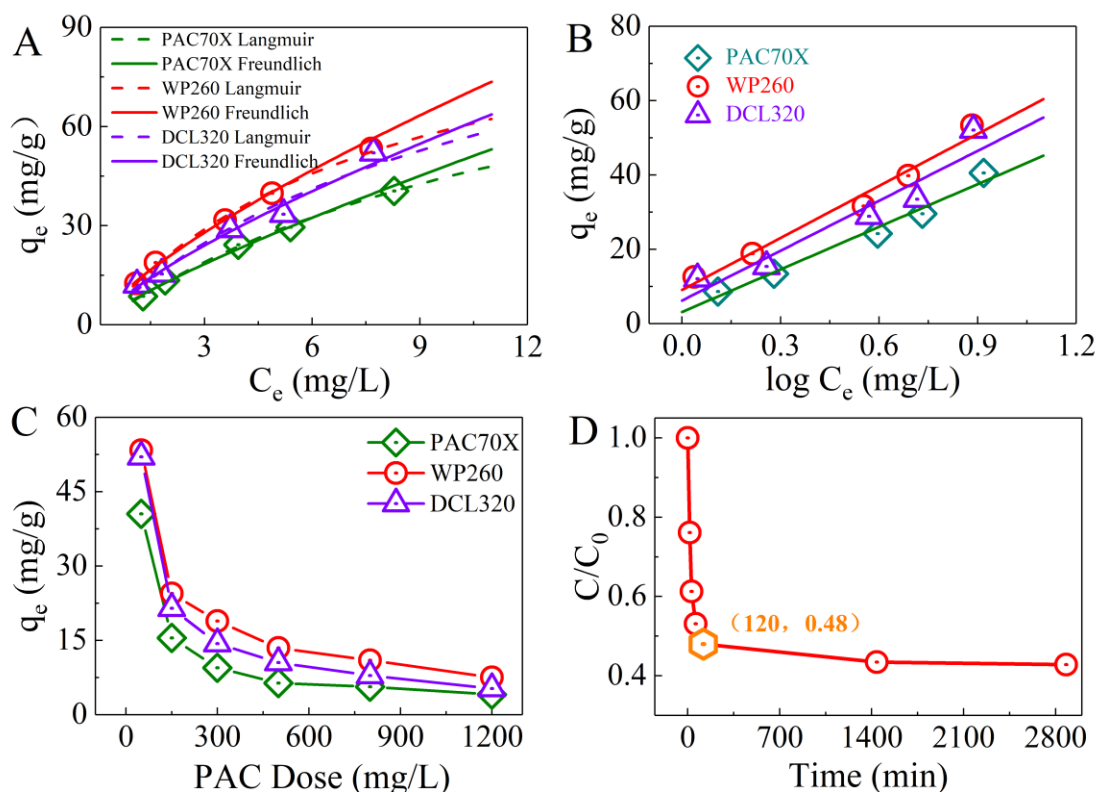
248 **3.1.1 Adsorption isotherms**

249 Fig. 1A-B depicts the isotherms for the adsorption of DOC onto PAC70X, WP260, and DCL320
250 adsorbents. To evaluate the maximum adsorption capacities of three types of PAC toward DOC,
251 the adsorption isotherms were obtained with the pH fixed at 7.5. The regression Freundlich,
252 Langmuir, and Temkin constants are presented in Table 3. The Freundlich isotherm equation
253 appears to be the most suitable one to describe the organic matter adsorption on PAC, yielding
254 R² values above 0.995. In the Freundlich model, there exists a distribution of sites with different
255 adsorption energies and more than one layer of adsorbates can adsorb onto the PAC. The value
256 of n is between 1 and 5, indicating that all three activated carbons favorably adsorb organic
257 matter from FPW. The value of $1/n$ for WP260 is the smallest, confirming that this material is
258 the most adequate one among the three options. In addition, a value below unity implies
259 chemisorption process (Foo and Hameed, 2010). Fig. 1C shows the results of adsorption
260 equilibria tests at 293 K. The value of q_e decreased sharply at low PAC content and approached
261 very small values close to zero for a dose larger than roughly 300 mg/L, even though not the
262 entire amount of DOC was removed from the liquid phase (see Table 1). This result is indicative
263 of the fact that the active sites of the adsorbents were not fully utilized and that the limiting
264 factor was not the dose or the type of PAC, but possibly the nature of the DOC in the system, a
265 fraction of which did not follow an equilibrium-driven partitioning with the adsorbent phase.

266 Among the various PACs, WP260 possessed the highest organics adsorption efficiency,
267 consistent with adsorption isotherms. Therefore, WP260 was selected for the hybrid system with
268 the most appropriate dose of 300 mg/L.

269 **3.1.2 Adsorption kinetics**

270 Fig. 1D shows the adsorption kinetics of DOC onto WP260. The adsorption was relatively fast
271 within the first two hours, reaching a relative DOC value of 0.48, while it slowed down
272 significantly after this time. The rapid initial adsorption regime may be attributed to the high
273 concentration gradient between the adsorbate in solution and that on the solid phase, as well as to
274 the high number of sites available for adsorption. Later during treatment, the adsorption becomes
275 diffusion-controlled and other phenomena, such as the aggregation of DOC molecules, may
276 reduce the kinetics of adsorption (Crittenden et al., 2012). Also, the affinity with PAC of DOC
277 fractions may be lower for organic molecules that are still in suspension at later stages of the
278 adsorption treatment. The experimental data were simulated using pseudo first-order and pseudo
279 second-order models to examine the controlling mechanism of PAC adsorption, e.g., physical
280 adsorption, mass transfer, and chemical reaction. As shown in Fig. S3 and Table S1 of the
281 Supporting Information, the adsorption kinetics of DOC on WP260 may be simulated well by a
282 pseudo-second-order kinetics model (correlation coefficients, $R^2 > 0.997$). The equilibrium
283 concentration of DOC predicted by the pseudo second-order model agrees well with the
284 experimental data, suggesting chemisorption as the rate-controlling step for the DOC adsorption
285 onto WP260, consistent with what discussed above.



286

287 **Fig. 1.** Adsorption equilibria, kinetics, and models. (A) Adsorption isotherms of DOC adsorbing
 288 from the coagulated FPW on different PACs (dose of 50 mg/L and total adsorption time of 48 h)
 289 and best fittings with Freundlich and Langmuir models. (B) Adsorption isotherms of DOC
 290 adsorbing from the coagulated FPW on different PACs (dose of 50 mg/L and total adsorption
 291 time of 48 h) and best fittings with Temkin model. (C) Comparison of adsorption equilibria of
 292 DOC from the coagulated FPW on different PACs for a total adsorption time of 48 h. (D)
 293 Kinetics of adsorption of DOC from the coagulated FPW, with a dose of WP360 of 300 mg/L.
 294 All the experiments were performed at pH 7.5 and at a temperature of 293 K.

295

296 **Table 3.** Isotherm fitting parameters for the adsorption of DOC from raw FPW onto WP260,
 297 DCL320, and PAC70X powdered activated carbon

Specifications	Freundlich			Langmuir			Temkin		
	1/n	K _F	R ²	Q _M	K _L	R ²	B	K _T	R ²
WP260	0.73	12.43	0.995	109.89	0.12	0.981	46.66	1.57	0.977
PAC320	0.75	10.54	0.987	120.48	0.09	0.758	44.75	1.38	0.913
DCL70X	0.82	7.51	0.992	112.36	0.070	0.960	38.23	1.21	0.981

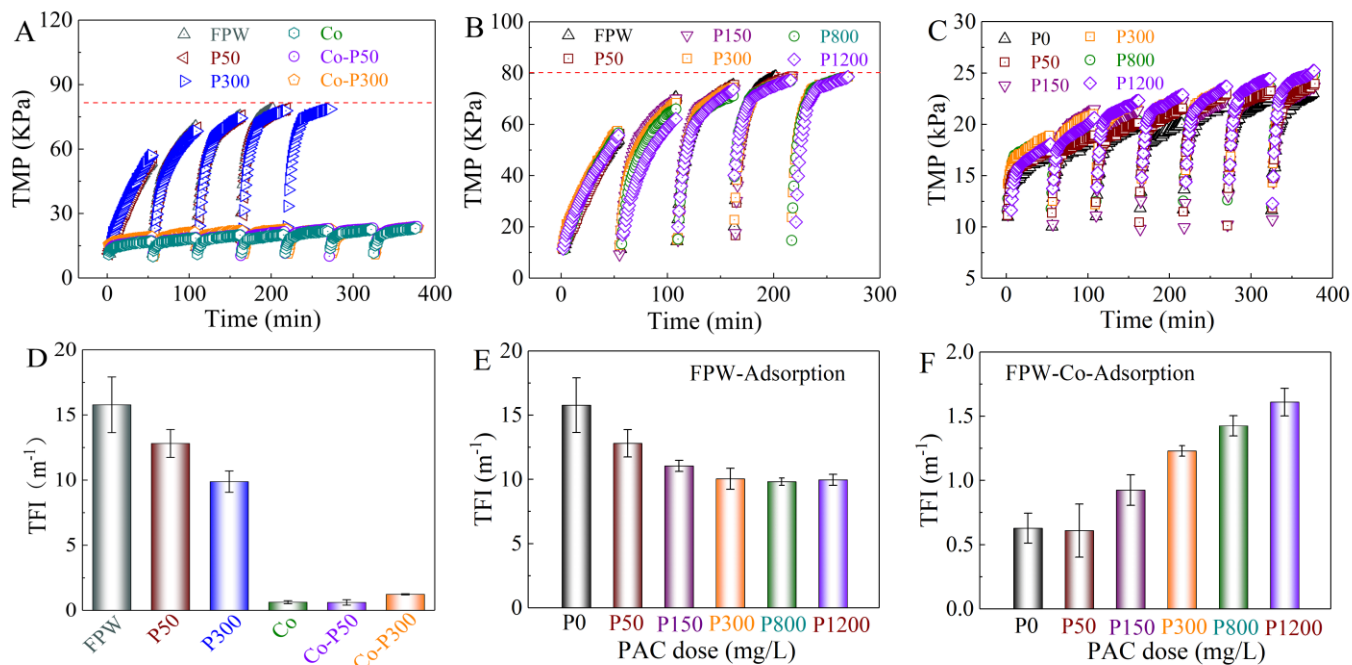
298

299 **3.2 Effect of pretreatment on fouling in ultrafiltration**

300 Various effluents were fed to the UF system to evaluate their fouling propensity, thus the
301 efficacy of feed pre-treatment. **In particular, different combinations of pre-treatment processes**
302 **were assessed, including coagulation alone, PAC adsorption alone, and a sequence of the above,**
303 **i.e., coagulation followed by adsorption.** The transmembrane pressure of the UF system during
304 the constant-flux treatment of FPW was monitored over time as an indication of membrane
305 fouling and is shown in Figure 2A-C. The same initial flux of 50 L m⁻²h⁻¹ was applied to all
306 experiments. Obviously, as the operating time increased, TMP also increased because of fouling.
307 The periodic hydraulic backwashing resulted in the discontinuous cycles shown in Figure 2. The
308 TMP was maintained lower than 80 kPa, as above this value the UF performance can deteriorate
309 (Jarzyńska and Pietruszka, 2011). As shown in Fig. 2A, the TMP increased significantly and
310 rapidly while treating FPWs that had not undergone previous coagulation, suggesting that
311 coagulation using aluminum coagulant can effectively reduce UF membrane fouling, which is in
312 accordance with our previous research (Chang et al., 2019b). The growth rate of the measured
313 TMP was also slowed down during the treatment of raw water filtered with a 0.45 μm pore-size
314 filter (Fig. S4): the TFI was reduced by 49.4% compared to the TFI when the raw water was
315 directly fed to the UF system. This result indicates that some large particulates and matter (>0.45

316 μm) can also increase the fouling of the UF membrane. Overall, the fouling rate decreased with
317 the following order of feed water: raw FPW, FPW subject to adsorption only, FPW subject to
318 microfiltration only, FPW subject to filtration and then adsorption, FPW subject to coagulation
319 and then adsorption (Fig. 2D).

320 When the raw FPW was only pre-treated by PAC, the UF membrane fouling decreased with
321 an increase in PAC dosage of 0-300 mg/L, as shown in Fig. 2B and E. Above the dosage of 300
322 mg/L, comparable UF fouling was observed up to 1,200 mg/L.. On the contrary, the opposite
323 effect with PAC dose was observed for FPWs that were first treated by coagulation (Fig. 2C, F).
324 There, fouling effects were significantly less critical than those observed for feed waters that
325 were only treated by adsorption without prior coagulation. However, the TMP increased slightly
326 with the increase in PAC dose. Indeed, as the PAC dose increased from 0 to 1200 mg/L, the TFI
327 increased from 0.63 to 1.61 (Fig. 2F). This observation may be rationalized as PAC particles and
328 gels accumulated on the surface to contribute in the formation of the fouling layer, as others have
329 previously reported (Cheng-Fang Lin 1999; Zhang et al., 2003). Therefore, while the
330 coagulation treatment helps remarkably in fouling reduction, the PAC should not be overdosed in
331 the following adsorption step. Coagulation removed particles and colloids in suspension (Kong
332 et al., 2017), preventing the formation of large settleable flocs with PAC. As such, PAC
333 remained in suspension and could foul the UF membrane, actually representing the dominant
334 factor in membrane fouling under these conditions.

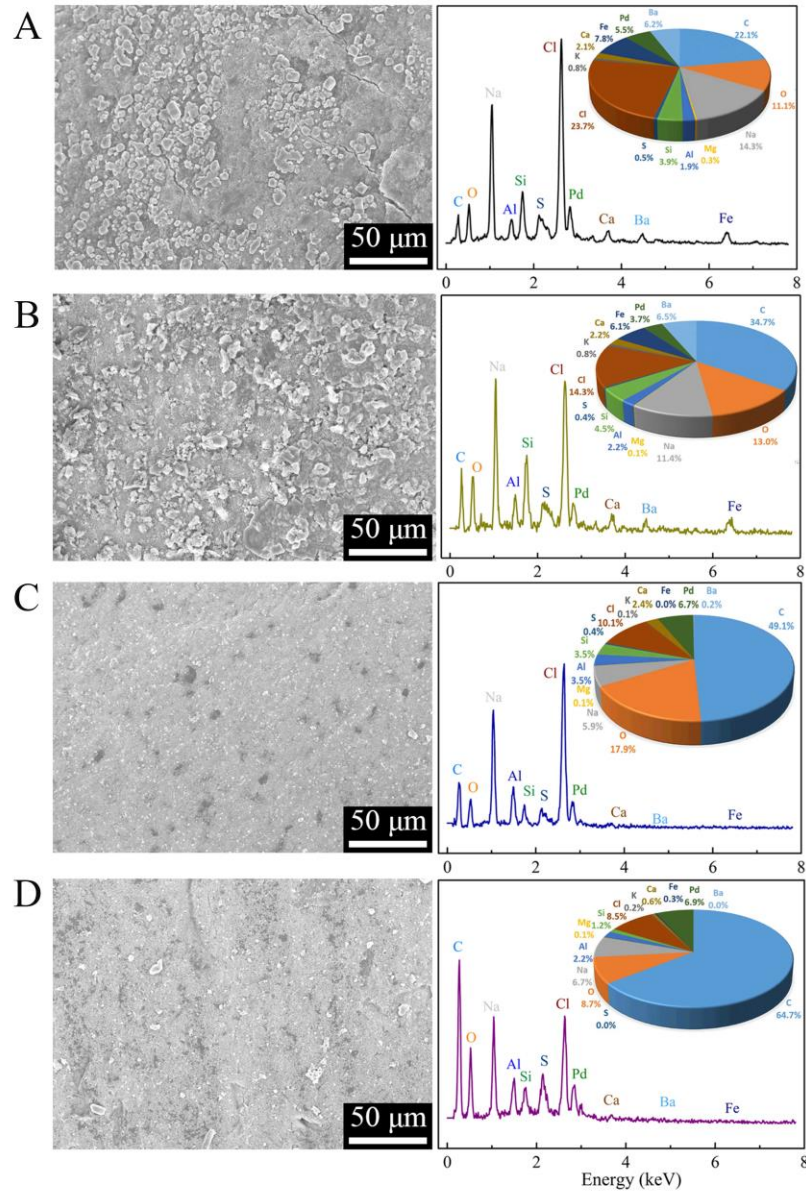


335
 336 **Fig. 2.** UF membrane fouling expressed as transmembrane pressure (TMP) and total fouling
 337 index (TFI). (A, B, C) TMP as a function of time and (D, E, F) TFI when the UF system was
 338 applied to treat (A, D) effluents from different pre-treatment processes, (B, E) effluents treated
 339 by PAC adsorption without prior coagulation for different doses of WP260, and (C, F) effluents
 340 treated by coagulation followed by PAC adsorption for different doses of WP260. The labels
 341 indicate the following: “FPW” for raw influent water, “Co” for coagulation only, “P” for
 342 adsorption. The numbers in the labels refer to different PAC doses.

343
 344 The FPW chemistry and fouling agents constantly change the membrane surface properties
 345 and membrane-foulant interactions during fouling (Bellona et al., 2004). To improve the
 346 understanding of UF performance with FPW, the fouled membranes and fouling layers were
 347 characterized. SEM-EDS analyses confirmed that the UF membrane surface was covered with a
 348 dense foulant layer following filtration of the raw FPW (Fig. 3A) or of FPW treated with

349 coagulation only (Fig. 3B). Specifically, the raw FPW created a thick and dense layer, consistent
350 with the results presented by Chang et al.(Chang et al., 2019b) By contrast, when coagulated-
351 adsorption water was treated in ultrafiltration (Fig. 3C, 3D), a thinner foulant layer covered the
352 membrane surface and not its entirety was covered by foulants. Also, irregular particles appeared
353 on the surface of the UF membrane when the adsorbent dose was 1200 mg/L compared to the
354 adsorbent dose of 300 mg/L, suggesting the presence of PAC particles for high doses. This
355 hypothesis is corroborated the relative content of carbon on the sample shown 4D (64.7%) was
356 significantly higher than on that relative to 4C (49.1%). In general, the EDS analysis showed a
357 large content of elements Cl, Na, C, and O, as well as high concentrations of Si, Ca, Mg, Al, S,
358 Fe, Sr, and Ba on the fouled UF membrane surface, compared with the new PVDF membrane
359 (Tab. S2). Although almost the same elements were detected on the surface of all the fouled
360 membranes, the relative amounts of the various elements differed. The relative weight
361 percentage of elements Mg, Ca, Fe, Ba decreased with the increase of WP260 dose, suggesting a
362 larger removal for higher PAC concentrations during adsorption. Remarkably, almost no Ca, Ba,
363 or Fe were detected on the surface of the UF membrane following treatment of water pretreated
364 by both coagulation and adsorption (Fig. 3C, 3D). Comparing Fig. 2 and Fig. 3, the TFI values of
365 the UF membrane were almost unchanged when fed with coagulation-adsorption treated water or
366 only coagulation-treated water (Fig. 2), but the nature of the foulants on the surface of these
367 membranes, provided by EDS analyses, is significantly different (Fig. 3). The results obtained in
368 this study were similar to those found in the published literature (Chang et al., 2015; Remize et
369 al., 2010). Although the total permeability could be almost completely restored, only part of the
370 foulants were removed from the membrane, with a certain amount of foulants still deposited on
371 the membrane surface.. In summary, the results presented in Fig. 3 and Fig. S5 of the Supporting

372 Information imply that coagulation combined with activated carbon adsorption has the potential
 373 to greatly reduce fouling, in turn improving the membrane performance.



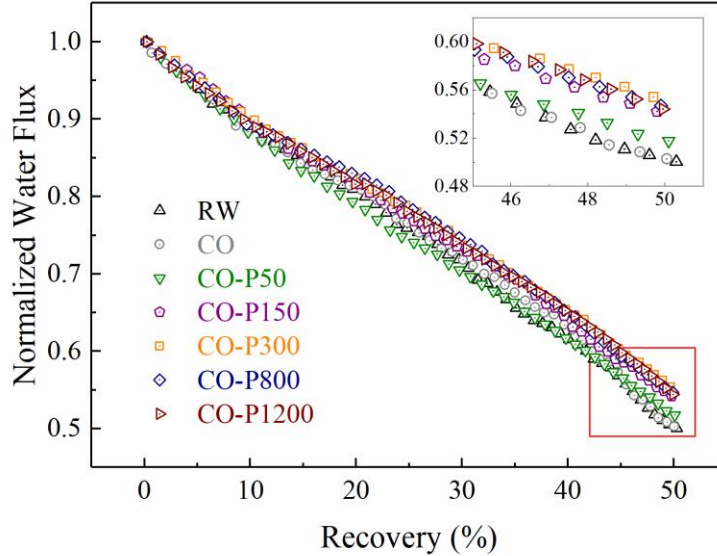
374

375 **Fig. 3.** SEM-EDS analyses of the UF membrane surface after fouling following the filtration of
 376 effluents that had been treated with different pre-treatment processes. UF filtration of the (A) raw
 377 FPW; (B) effluent from coagulation; (C) effluent from coagulation and adsorption at the WP260

378 dose of 300 mg/L, and (D) effluent from coagulation and adsorption at the WP260 dose of 1200
379 mg/L. All the experiments performed at constant flux of 50 LMH and temperature of 293 K.

380 **3.3 Effect of pretreatment on fouling in reverse osmosis**

381 The normalized water flux decline with different feed solutions of the RO process operating up
382 to 50% recovery is presented in Fig. 4. The permeate flux decreased with increasing recovery,
383 which is mainly due to the increase in the osmotic pressure of the retentate. In general, the
384 measured flux across the membrane was higher for larger PAC doses applied in the adsorption
385 pre-treatment. This effect was observed up to a PAC dose of 300 mg/L, above which the RO flux
386 was not function of the adsorption conditions. Specifically, adsorption pre-treatment performed
387 with 300 mg/L of WP260 reduced the fouling in RO and increased flux by 10.8%. **This was**
388 **mainly due to the difference in the influent water quality of the RO. In terms of organic matter**
389 **(DOC, UV₂₅₄) and turbidity, PAC at a dosage of 300 mg/L could ensure that the influent water**
390 **quality of the RO had basically the lowest concentration of pollutants, as discussed in detail in**
391 **Section 3.4.** In addition, the positive effect of adsorption is expected to be even more pronounced
392 for longer operating time and if cross-flow filtration is used instead of dead-end mode (Quay et
393 al., 2018).



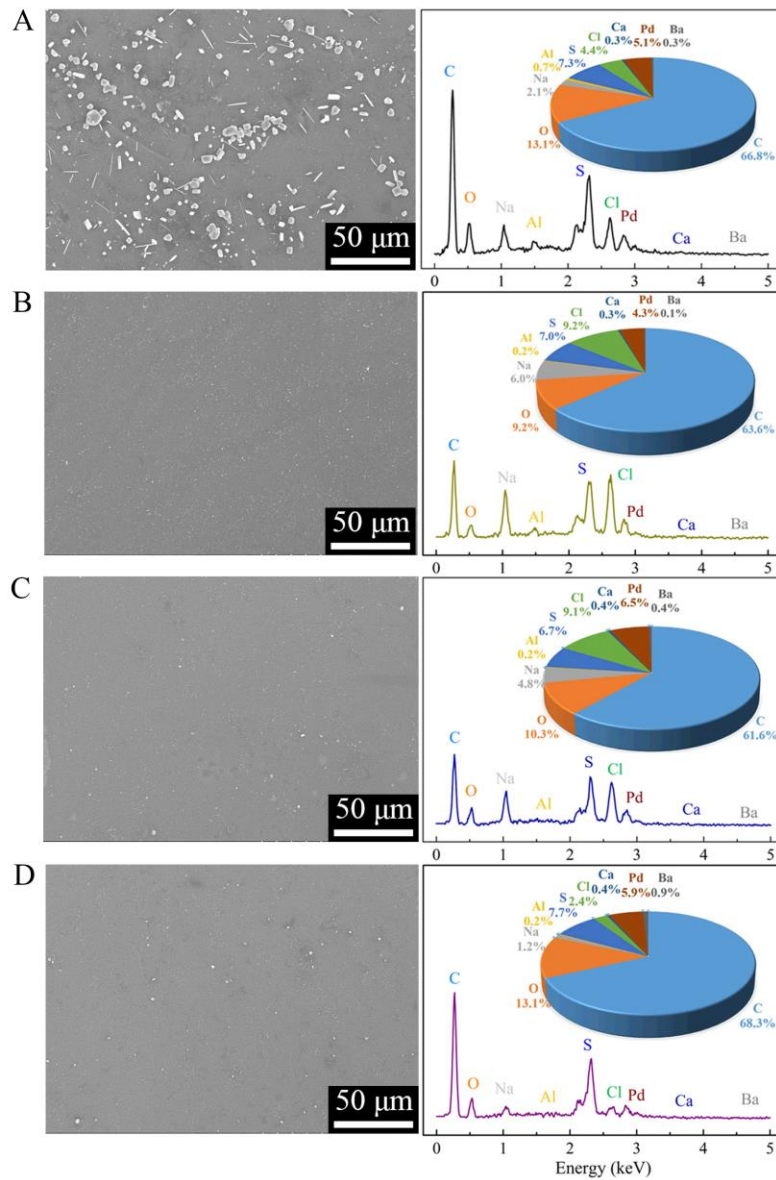
394

395 **Fig. 4.** Normalized water flux during RO desalination as a function of recovery for feed water
 396 following UF treatment and that that had been subject to different pre-treatment processes. The
 397 applied pressure was 5.5 MPa and the temperature during RO filtration was 293 K.

398

399 The surface morphology and elemental composition of the fouling layer was analyzed on RO
 400 membranes following the treatment of effluents from the UF step that were subject to different
 401 pre-treatments. The results from SEM-EDS analyses are shown in Fig. 5. C, O, and S are the
 402 main elements observed on the surface of the RO membranes, similarly to the pristine membrane
 403 (Tab.S2). Nevertheless, numerous particles of mostly CaCO_3 and to a less extent of BaCO_3 were
 404 visible on the membrane fed with the raw FPW only treated by UF (Fig. 5A), as also shown in a
 405 previous report (Guo et al., 2018). The presence and the size of these crystals was significantly
 406 reduced when the water was pre-treated by coagulation (Fig. 5B). **This effect is caused by**
 407 **coagulation, which reduced the pH and slowed down the precipitation of calcium carbonate.**
 408 When PAC adsorption was applied, either at a concentration of activated carbon of 300 mg/L or

409 1200 mg/L, only trace amounts of Ca and Ba were present on the surface of the membrane. In
 410 this case, the pH, alkalinity and Ca²⁺ concentration were all key factors affecting the CaCO₃
 411 scaling of the RO membrane (Table S3). These observations confirm the effectiveness of
 412 coagulation and PAC adsorption also to reduce scaling in the final RO step.



413
 414 **Fig. 5.** SEM-EDS analyses of the RO membrane surface after fouling following the desalination
 415 of UF effluents that had been treated with different pre-treatment processes. RO desalination of

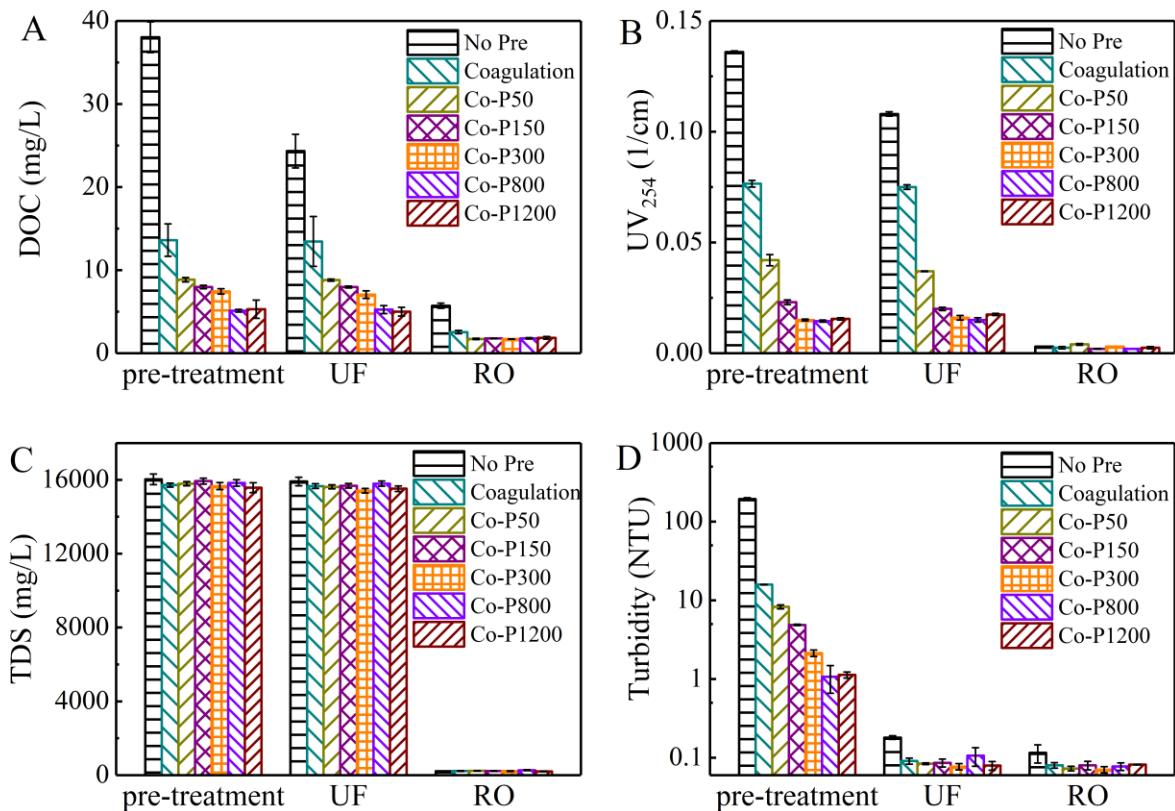
416 the UF permeate from the treatment of the (A) raw FPW; (B) effluent from coagulation; (C)
417 effluent from coagulation and adsorption at the WP260 dose of 300 mg/L, and (D) effluent from
418 coagulation and adsorption at the WP260 dose of 1200 mg/L. All the experiments performed at
419 an applied pressure of 55 bar, final recovery of 50%, and temperature of 293 K.

420

421 **3.4 Quality of the effluents and of the final water stream**

422 Fig. 6 summarizes the removal rates of different classes of contaminants exiting the adsorption
423 step, the ultrafiltration step, and the reverse osmosis steps, when the treatment units were
424 challenged by waters pretreated by different processes. Coagulation reduced the DOC by 64.2%,
425 and the addition of 300 mg/L PAC further reduced this parameter by 48.5%. In addition,
426 coagulation had a good removal effect (91.6%) on turbidity. Adsorption following coagulation
427 could further remove turbidity and reduce the turbidity of the effluent to a value below 10 NTU.
428 The removal of DOC, UV₂₅₄, and turbidity typically increased at higher dosages of PAC.
429 However, very similar removals were observed for PAC amounts of 300 mg/L and 1200 mg/L,
430 suggesting that 300 mg/L was the optimal dose for PAC adsorption of FPW, a result that is in
431 complete accordance with the results of membrane fouling. The same organic removal rate
432 previously observed by James et al. was achieved in this study but with roughly half the dose of
433 PAC (Rosenblum et al., 2016). It should be noted that when the raw FPW was directly fed to the
434 UF step, both the DOC and the UV₂₅₄ were significantly reduced in this step, possibly because
435 the large particulates adhered to some organic matter, thus helping in its removal. However,
436 feeding the UF directly with non-pretreated FPW is not a viable option, as discussed above and
437 based on fouling results. As expected, UF abated the turbidity while it had negligible removal of
438 ions. Finally, RO removed TDS very efficiently. Overall, the best system combining all the

439 treatment steps, i.e., coagulation followed by adsorption with 300 mg/L of PAC followed by UF
 440 and RO, achieved a total ion reduction of more than 98.6%, and a DOC removal rate of 95.5%.
 441 The quality of this effluent, also summarized in the rightmost column of Table 1, reached the
 442 strict reuse standards for beneficial drilling applications and irrigation (Alzahrani and
 443 Mohammad, 2014). In addition, the cost data for each process unit (Table S4) are presented in
 444 the SI based on the relevant literature. The cost of the coagulation-adsorption-UF-RO process is
 445 lower than other FPW treatment schemes including, for example, FO or mechanical vapor
 446 compression. Therefore, the scheme proposed here has potential for the treatment of shale gas
 447 FPW in China in the future.



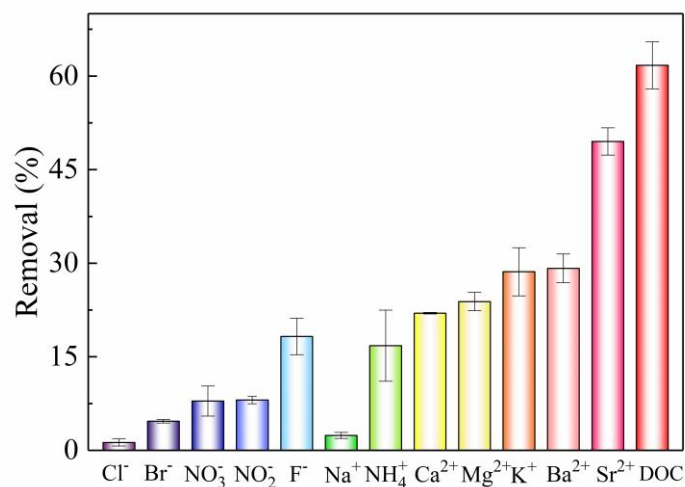
448

449 **Fig. 6.** Contents of different contaminants, specifically, (A) DOC; (B) UV₂₅₄; (C) TDS; and (D)

450 turbidity obtained at different stages of the treatment systems and for effluents that were pre-
451 treated by different processes. The label “No Pre” indicates raw water without any pre-treatment.

452 **3.5 Ion removal during activated carbon adsorption**

453 Although coagulation, adsorption, and UF did not remove TDS at a significant rate, it is of
454 further interest to evaluate the ability of pre-treatments to remove some specific ions from FPW.
455 The effect of coagulation and UF on specific ion removal was previously studied (Chang et al.,
456 2019b; Guo et al., 2018). Here, we focus on the removal rates of different ions from the
457 coagulated FPW by adsorption, presented in Figure 7. The results indicate a competition effect
458 for the adsorption of cations, whereby the removal rate may be ranked in the following ascending
459 order: Na^+ (2.4%) < NH_4^+ (16.8%) < Ca^{2+} (22.0%) < Mg^{2+} (23.9%) < K^+ (28.6%) < Ba^{2+}
460 (29.2%) < Sr^{2+} (49.5%) < DOC (61.7%). The removal rate of anions may be instead arranged in
461 the order: Cl^- (1.3%) < Br^- (4.7%) < NO_3^- (7.9%) < NO_2^- (8.1%) < F^- (18.3%) < DOC
462 (61.7%). Clearly, the removal of divalent ions was greater than that of monovalent ions, as the
463 adsorption of negatively charged DOC promotes the concurrent removal of cations associated
464 with the organic molecules electrostatically or by complexation (Foo and Hameed, 2010; Gao et
465 al., 2018). Interestingly, the removal of K^+ was higher than for other divalent cations known to
466 interact favorably with organic matter, such as calcium. This result may be partially rationalized
467 with the overall larger size of K^+ , which are thus associated with a more favorable energy of
468 adsorption (Neugebauer and Scheffler, 1992). Finally, the kinetics of removal of the various ions
469 by adsorption are presented in Fig. S6.



470

471 **Fig 7.** Removal rates of DOC, anions, and cations during the adsorption step with WP260
 472 powdered activated carbon at the dose of 300 mg/L. **The adsorbate was coagulated FPW.**

473 **4. Conclusions**

474 Shale gas flowback and produced water, as a complex mixture of fracturing fluid and formation
 475 water, may be effectively reused if appropriately treated. **This study provides a new FPW**
 476 **treatment train consisting of coagulation, adsorption followed by UF and RO desalination.** In
 477 particular, this work focused on the mechanism of adsorption and on the effects of pre-treatment
 478 on effluent quality and membrane fouling control. The following main conclusions can be drawn
 479 from the results:

- 480 1. The overall system performed a reliable treatment of the specific FPW to obtain a high-
 481 quality product water with characteristics compatible with its reuse. Therefore, this study
 482 provides a potential reference for a centralized shale gas FPW treatment plant in the Sichuan
 483 Basin of China.

484 2. Coagulation and adsorption are valid pre-treatment for membrane processes. Interesting
485 patterns were observed: when PAC was directly applied to adsorb contaminants from the raw
486 FPW, the UF membrane fouling decreased with increasing PAC dosage. However, when
487 coagulation was added before adsorption, UF membrane fouling increased with increasing PAC
488 dosage. However, in this latter case, membrane fouling was much smaller than when UF was
489 applied to an effluent pre-treated only by adsorption. Therefore, adsorption should be preceded
490 by coagulation for improved performance of the system.

491 3. There was an optimal activated carbon dosage of 300 mg/L for the adsorption treatment.
492 This dose resulted in the greatest gain in terms of fouling reduction in both UF and RO and in
493 terms of quality of the final product water.

494 4. During the adsorption process, ions were removed at different rates, also due to co-sorption
495 of cations with the organic matter. The mechanism of the adsorption of ions by PAC in FPW
496 needs further research.

497

498 **Appendix A. Supplementary material**

499 The supporting information is available free of charge.

500 The size distributions of three adsorbents; linear plots of pseudo first order and pseudo second
501 order adsorption kinetics of DOC on WP260; summary of adsorption kinetic parameters; EDS
502 analyses of the new UF and RO membranes surface.

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511

512

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