

1 **Comparison of different coagulants to improve membrane distillation**
2 **performance for landfill leachate concentrate treatment**

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15 **Abstract**

16 This study investigated the impacts of different coagulants on the performance of
17 membrane distillation (MD) for landfill leachate concentrate treatment. Three common
18 coagulants, including polyaluminum chloride (PAC), polyferric sulfate (PFS), and ferric
19 chloride (FeCl_3), were compared at different dosages. MD performance was then
20 evaluated regarding both contaminant retention and membrane fouling in the treatment
21 of coagulated leachate concentrate. Results show that the three coagulants exhibited
22 desirable performance for floc formation and thus the removal of organic matter, mainly
23 humic substance (> 80% as indicated by total organic carbon) at the dosage of 1200 mg/L.
24 As such, coagulation enhanced MD performance for contaminant removal and fouling
25 mitigation with the highest increase in ammonium retention from 48.3% to 90.1%. Of the
26 three coagulants, PFS was more effective to improve MD capability for the retention of
27 heavy metals and volatile organic compounds. Furthermore, PFS could synergistically
28 remove organic and inorganic foulants (e.g. humic acid, calcium, and magnesium ions)
29 in the coagulation of landfill leachate concentrate to alleviate membrane fouling in
30 subsequent MD operation.

31 **Keywords:** Landfill leachate concentrate; membrane distillation; coagulation;
32 contaminant removal; membrane fouling

33 1 Introduction

34 Sanitary landfilling is a low cost and simple method for managing municipal solid
35 waste.^{1,2} In a sanitary landfill, leachate is collected for treatment and resource recovery.
36 The leachate is commonly generated from rainwater ingress to the landfill and the
37 decomposition of organic solid wastes under anaerobic and/or anoxic conditions. Landfill
38 leachate has a high content of organic matter, inorganic salts, and toxic substances, such
39 as heavy metals.³ Therefore, advanced treatment techniques, including anaerobic and
40 aerobic bioprocesses, membrane separation, and oxidation processes, are often used to
41 treat landfill leachate.⁴⁻⁷ High pressure membrane processes, such as nanofiltration (NF)
42 and reverse osmosis (RO), are also used to further purify effluent from bioprocesses for
43 the recycling and/or discharge of high-quality water.^{8,9} Nevertheless, retentate from
44 NF/RO, which is also known as landfill leachate concentrate, with the enrichment of toxic
45 substances needs further disposal to avoid severe environmental impacts.¹⁰

46 Several advanced techniques have been developed and practiced for the further treatment
47 of leachate concentrate. These mainly include mechanical vapor compression,
48 incineration, chemical oxidation, and membrane concentration.¹¹ Of these techniques,
49 membrane distillation, which is a combination of thermal evaporation and membrane
50 separation, has extracted significant interest given its low energy consumption and simple
51 operation.^{12,13} Chen *et al.*¹⁴ investigated the performance of direct contact membrane
52 distillation (DCMD) for the treatment of landfill leachate concentrate and observed more
53 than 98% retention of organic matter as indicated by total organic carbon (TOC) and total
54 nitrogen (TN). Nevertheless, the enrichment of organic matter, such as humic acid from
55 upstream biological treatment processes, and inorganic salts, particularly calcium (Ca^{2+})
56 and magnesium (Mg^{2+}), in leachate concentrate can lead to severe membrane fouling and
57 wetting in MD operation.¹⁵ Jia *et al.*¹⁶ reported that both water flux and salt retention
58 decreased significantly when DCMD was used to reduce the volume of landfill leachate
59 concentrate by 5 times.

60 Coagulation has been widely used for wastewater pretreatment to mitigate fouling in
61 subsequent membrane purification. Li *et al.*¹⁷ demonstrated that the addition of
62 polyaluminum chloride (PAC) could effectively remove suspended solids (SS) and
63 dissolved organic matter (DOM) in the coagulation of coking wastewater to enhance the
64 water flux of subsequent MD process by 25%. Shi *et al.*¹⁸ reported that the water flux of
65 DCMD was increased by 74% after coagulation pretreatment of landfill leachate
66 concentrate using hydroxide/polyacrylamide (PAM). However, aggravation on MD
67 membrane fouling was also observed in several studies when integrated downstream for
68 coagulated effluent treatment although investigation related to landfill leachate
69 concentrate treatment is still rare. For instance, Sanmartino *et al.*¹⁹ reported that hydroxide
70 was used to treat the reverse osmosis brine but the water flux of DCMD was reduced by
71 more than 25% when the operating time was 7 hours. Thus, further investigation is needed
72 to screen suitable coagulants to integrate coagulation and MD to advance landfill leachate
73 concentrate treatment.

74 This study aims to comprehensively compare the effects of different coagulants on MD
75 performance for landfill leachate concentrate treatment. Three common coagulants,
76 including ferric chloride (FeCl₃), PAC and polyferric sulfate (PFS), were selected for the
77 pretreatment of landfill leachate concentrate. Water flux and contaminant removal were
78 further determined to evaluate the advancement in MD performance by coagulation.
79 Furthermore, surface morphology and chemical characteristics were qualified to elucidate
80 the effects of coagulation on MD membrane fouling. Results from this study facilitated
81 the development of coagulation-assisted MD process for low-cost treatment of landfill
82 leachate concentrate to improve the environmental benefits of sanitary landfill for solid
83 waste management.

84 **2 Materials and methods**

85 ***2.1 Leachate concentrate***

86 Landfill leachate concentrate was collected from a local landfill leachate treatment plant

87 (Beijing, China). In this treatment plant, landfill leachate was disposed by a series of
 88 biological, chemical, and physical processes, including anaerobic digestion, anoxic and
 89 oxic activated sludge treatment, and membrane bioreactor (MBR) equipped ultrafiltration
 90 (UF) (Fig. 1A). The MBR effluent was purified by nanofiltration (NF) and reverse
 91 osmosis (RO). The NF and RO concentrates were further concentrated by UF and RO for
 92 volume reduction. Landfill leachate concentrate used in this study was sampled from the
 93 first stage of NF and RO retentates and then mixed for storage at 4 °C until experiment.
 94 The basic physicochemical characteristics of the mixed leachate concentrate are shown
 95 in Table 1.

96 **Table 1:** Basic physicochemical characteristics of landfill leachate concentrate (values
 97 are mean \pm standard deviation of three replicate samples)

Parameters	Value	Parameters	Value
pH	7.6 \pm 0.2	K ⁺ (mg/L)	4118.3 \pm 98.9
EC (mS/cm)	46.3 \pm 0.2	Ca ²⁺ (mg/L)	90.0 \pm 1.8
TOC (mg/L)	887.0 \pm 5.9	Mg ²⁺ (mg/L)	420.7 \pm 10.3
TN (mg/L)	3820.0 \pm 25.0	Cl ⁻ (mg/L)	7942.4 \pm 98.9
NH ₄ ⁺ -N (mg/L)	13.8 \pm 1.0	NO ₃ ⁻ -N (mg/L)	2747.64 \pm 32.6
Na ⁺ (mg/L)	7114.4 \pm 125.2	Turbidity (FTU)	2.9 \pm 0.1

98 **2.2 Experimental systems and protocol**

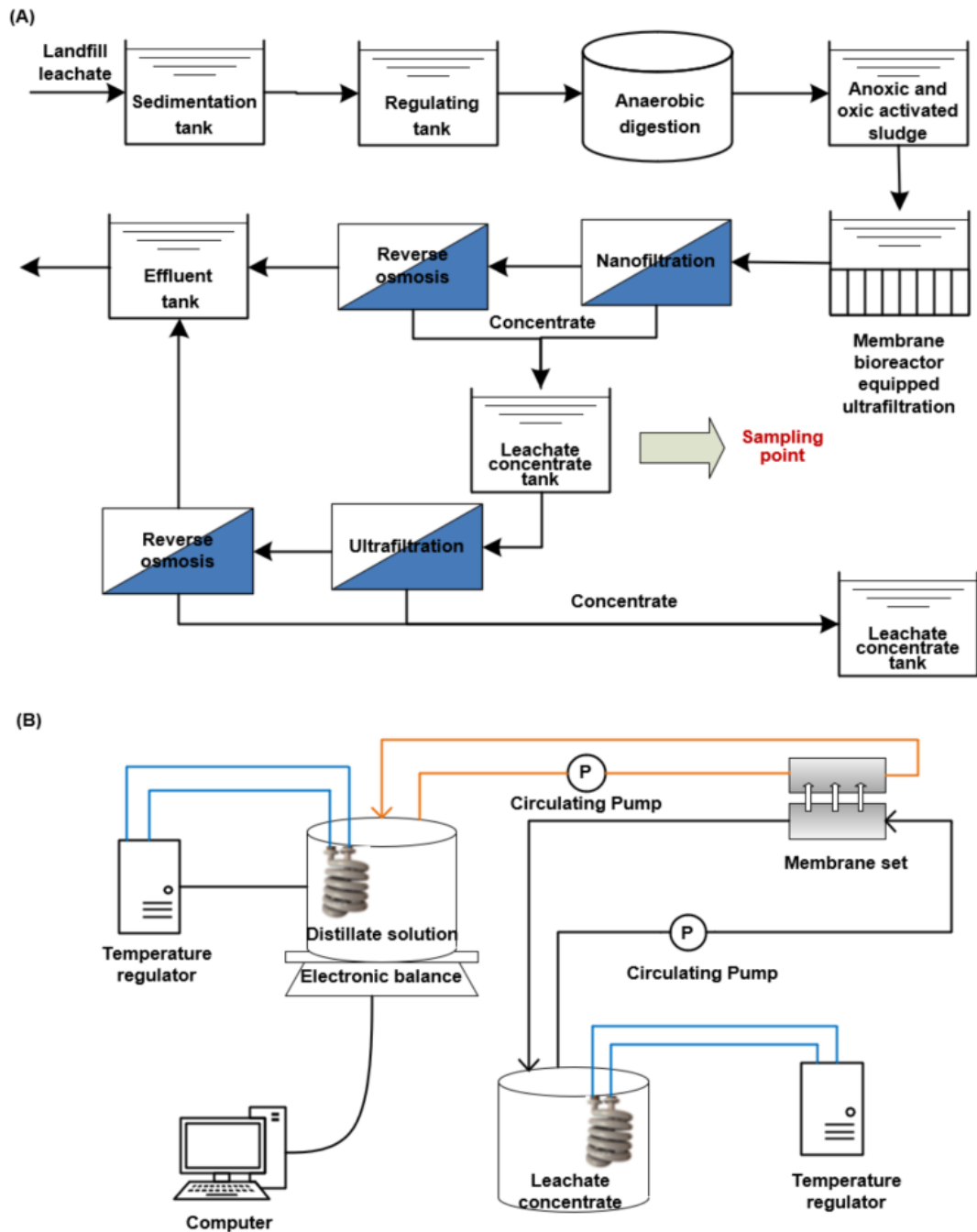
99 **2.2.1 Coagulation of landfill leachate concentrate**

100 Coagulation of landfill leachate concentrate was conducted using a set of six-paddle
 101 agitation device (JJ-6A, Suzhou Weir Laboratory Supplies, China). Landfill leachate
 102 concentrate (200 mL) was sampled into a series of 500 mL beakers. PAC, PFS and FeCl₃
 103 purchased from Shanghai Yuanye Bio-Technology were added to the beakers with an
 104 increase in dosage from 600 to 1600 mg/L for coagulation. Cationic polyacrylamides
 105 (CPAM) with the molecular weight in the range of 8 – 10 million was obtained from

106 Shanghai Macklin Biochemical Technology and then added at 0.8 mg/L to aid coagulation.
107 It has been reported that CPAM could effectively improve wastewater coagulation via
108 chemical coagulants given the adsorption and bridge of micro-flocs.²⁰ Landfill leachate
109 concentrate was stirred rapidly at 250 r/min for 2 min and then stirred slowly at 60 r/min
110 for 10 min before natural settlement for approximately 30 min at the room temperature
111 (25 ± 2 °C). All coagulation tests were triplicated.

112 ***2.2.2 Membrane distillation of coagulated leachate concentrate***

113 Leachate concentrate after coagulation was processed for DCMD using a lab-scale set-up
114 (Fig. 1B). The DCMD system consisted of a membrane module, a temperature regulator,
115 and two circulating pumps. The membrane set was assembled by two acrylic plates (10
116 cm × 6 cm) of 2 cm in thickness with etched flow channels to contribute an effective
117 membrane area of 50 cm². Polytetrafluoroethylene (PTFE) membranes with the average
118 pore size of 0.2 μm and porosity of 80% were purchased from Shanghai Mosu Scientific
119 Equipment and used for all tests. The PTFE membrane was placed in the middle of the
120 two plates to separate the flow of feed and distillate solutions. Each acrylic block was
121 etched to create a flow channel with 2 mm in depth, 50 mm in width, and 100 mm in
122 length. The initial volume of feed solution (i.e. coagulated landfill leachate) and distillate
123 solution (deionized water) was 500 and 300 mL respectively. Two circulating pumps
124 (WT600-2J, Longer, China) were used to simultaneously transfer the feed and distillate
125 solution to their respective channels at the cross-flow velocity of 1.7 cm/s. The heater and
126 chiller regulators were used to maintain the feed and distillate temperature at 50 ± 1 °C
127 and 20 ± 1 °C, respectively. The distillate tank was placed on a digital balance
128 (AX420ZH/E, AUX, USA) to record the weight change for flux calculation. Each MD
129 operation for the concentration of coagulated leachate concentrate was terminated until
130 the flux decrease to the negligible level (i.e. maximum water recovery). All MD tests were
131 triplicated.



132

133 **Fig. 1:** Sampling point to collect landfill leachate concentrate for experiments (A) and
 134 schematic diagram of the lab-scale membrane distillation system (B).

135 2.3 Analytical methods

136 2.3.1 Water quality measurement

137 TN and TOC were determined by a TOC/TN analyzer (TOC-VCSH, Shimadzu, Japan).

138 Ammonia nitrogen ($\text{NH}_4^+\text{-N}$), Mg^{2+} and Ca^{2+} were determined by a flow injection

139 analyzer (AA3, Seal, Germany) and an ion chromatograph (Aquion, ThermoFisher, USA),
140 respectively. Heavy metals, including arsenic (As), chromium (Cr), and lead (Pb), were
141 measured by an inductivity coupled plasma-optical emission spectrometer (ICP-OES,
142 iCAP 7000, Thermo, USA). DOM was characterized using a three-dimensional
143 excitation-emission matrix (3D-EEM) fluorescence spectroscopy (LS-55, Perkin, USA).
144 Volatile organic compounds (VOCs) were determined using a gas chromatography-mass
145 spectrometer (GC-MS, 7890A-5975C, Agilent, USA). Leachate concentrate samples
146 were acidified to pH of 2 using 0.2 mol/L H₂SO₄. The samples were extracted twice using
147 10 mL of dichloromethane (CH₂Cl₂) and then concentrated by a nitrogen blowing
148 instrument after dehydration. The GC-MS peak areas were compared with the NIST 17
149 database to identify organic components and relative contents.

150 *2.3.2 Membrane fouling analysis*

151 Given nonhomogeneous fouling layers on the MD membranes, two coupons with visible
152 foulants were cut for characterization.²¹ Membrane hydrophobicity was indicated by
153 contact angle tests using a contact angle meter (SL100B, NIKO, USA) with the
154 measurements of five water drops on each coupon.²² The morphology and element of
155 fouled membrane were pictured by a scanning electron microscope-energy dispersive
156 spectroscopy (SEM-EDS, Hitachi SU-8010, Japan). Attenuated total reflectance-Fourier
157 transform infrared spectrum (ATR-FTIR, Specturm RX-I, Perkin Elmer) was performed
158 to analyze the functional groups of membrane fouling layer.

159 *2.4 Statistical analyses*

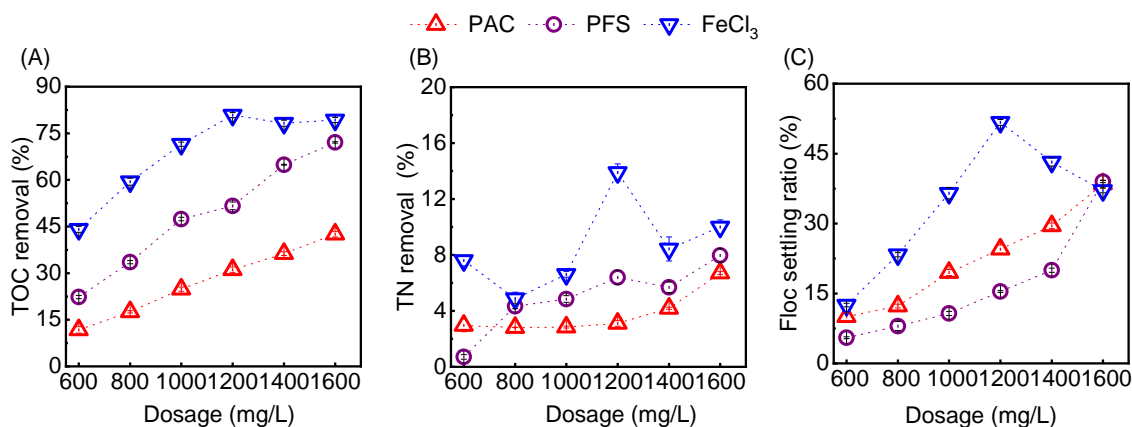
160 Significance among different results were analyzed by SAS 9.4 System. Origin 2022b
161 was used to complete the graphs.

162 **3 Results and discussion**

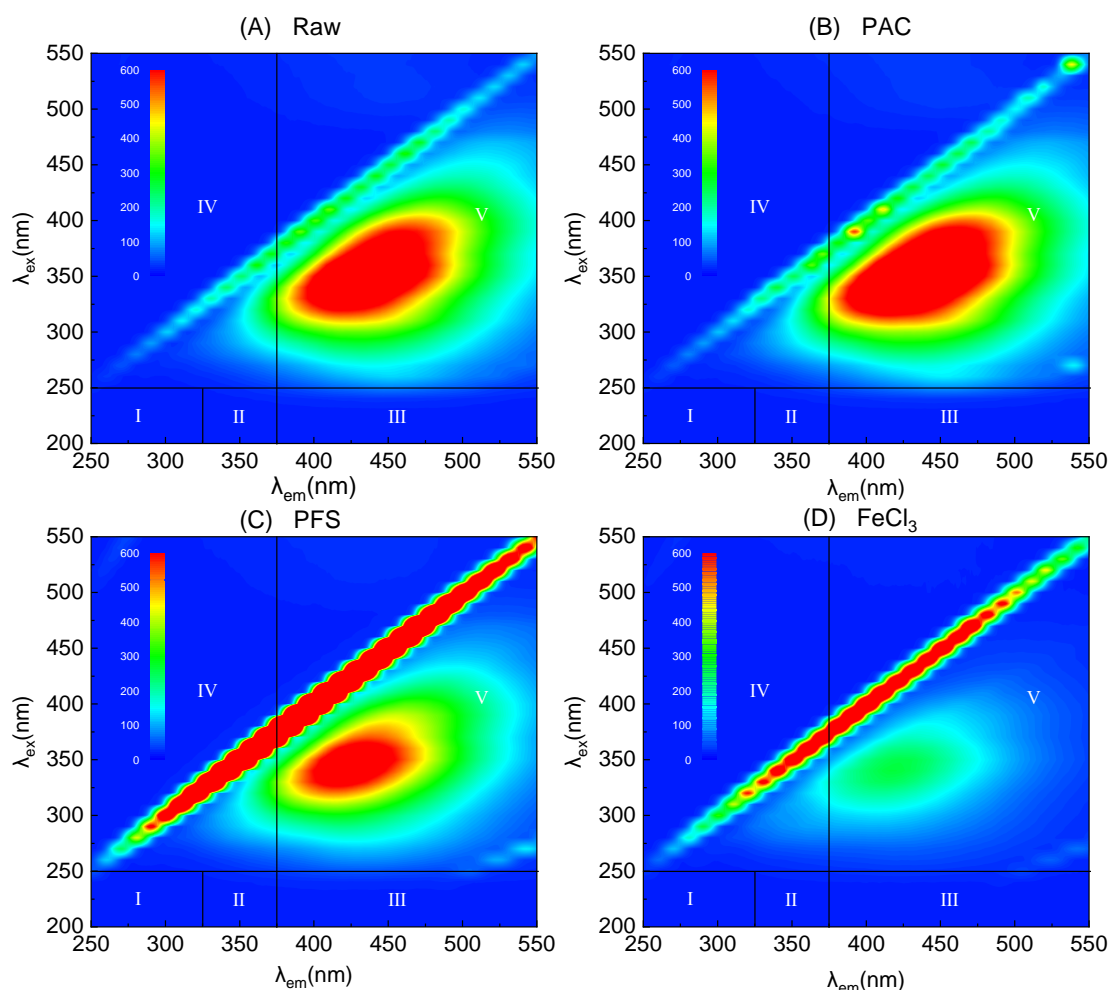
163 *3.1 Effect of coagulation on physicochemical properties of leachate concentrate*

164 In general, organic removal increased at increasing coagulant dosage (Fig. 2). At any

165 dosages, FeCl₃ exhibited higher removal of organic matter than PFS and PAC as indicated
 166 by both TOC and TN concentrations (Fig. 2). The highest removals of TOC and TN of
 167 80.8% and 13.9%, respectively, were achieved at 1200 mg/L FeCl₃. Similar results have
 168 also been reported by Zhao *et al.*²³ in the pretreatment of humic acid-kaolin synthetic
 169 wastewater and could be attributed to the addition of FeCl₃ to release more hydrogen and
 170 oxygen active groups (Fig. S1, Supplementary Data) via Fe hydrolysates to strengthen
 171 the adsorption of organic substances.²⁴ As such, the performance of all three coagulants
 172 for TOC and TN removal could be enhanced with an increase in their dosages until 1200
 173 mg/L to provide more Fe and Al ions for precipitation. It is noted that a small decrease in
 174 TN removal was observed with an increase in FeCl₃ dosage from 600 to 800 mg/L (Fig.
 175 2B). Further analysis indicated that such decrease was statistically insignificant ($P > 0.05$)
 176 and could be attributed to slight variation in the physicochemical characteristics of
 177 leachate concentrate in storage. Further analysis by EEM evidenced that the removal of
 178 organic matter by coagulation could be mainly attributed to the reduction of humic acid
 179 (Fig. 3). It has been reported that metal coagulants, particularly Fe ions, could interact
 180 with humic acid due to active hydroxyl groups on the surface of Fe hydrolysates.²⁵



181
 182 **Fig. 2:** Removal of (A) TOC, (B) TN, and (C) floc settling ratio by coagulation at different
 183 dosages. Three coagulants, including PAC, PFS and FeCl₃, were added to leachate
 184 concentrate and then mixed rapidly at 250 r/min for 2 min, slowly at 60 r/min for 10 min
 185 before natural settlement for approximately 30 min under the room temperature.



186

187 **Fig. 3:** 3D-EEM spectra of (A) raw and coagulated leachate concentrate by (B) PAC, (C)
 188 PFS and (D) FeCl₃ at 1200 mg/L. Experimental conditions are shown in the caption of
 189 Fig. 2.

190 Compared to TOC, much lower removal of TN (less than 14%) was observed for all three
 191 coagulants. This observation could be ascribed to the positively charged NH₄⁺-N in TN
 192 in the landfill leachate concentrate, which was difficult to be removed by coagulation
 193 through electrical neutralization or adsorption given electrostatic repulsion.²⁶ Of the three
 194 coagulants, FeCl₃ led to slightly higher TN removal from landfill leachate concentrate,
 195 possibly due to its release of more hydrogen reactive groups to generate more ferric
 196 hydroxide for enhanced adsorption.²⁴ It is noteworthy that no significant increase in TOC
 197 removal but a decrease in TN removal occurred when the dosage of FeCl₃ exceeded 1200
 198 mg/L. Such results were possibly due to relatively low TOC residue (Fig. S2,

199 Supplementary Data) for removal and the release of nitrogen species during floc
200 restabilization.²⁷

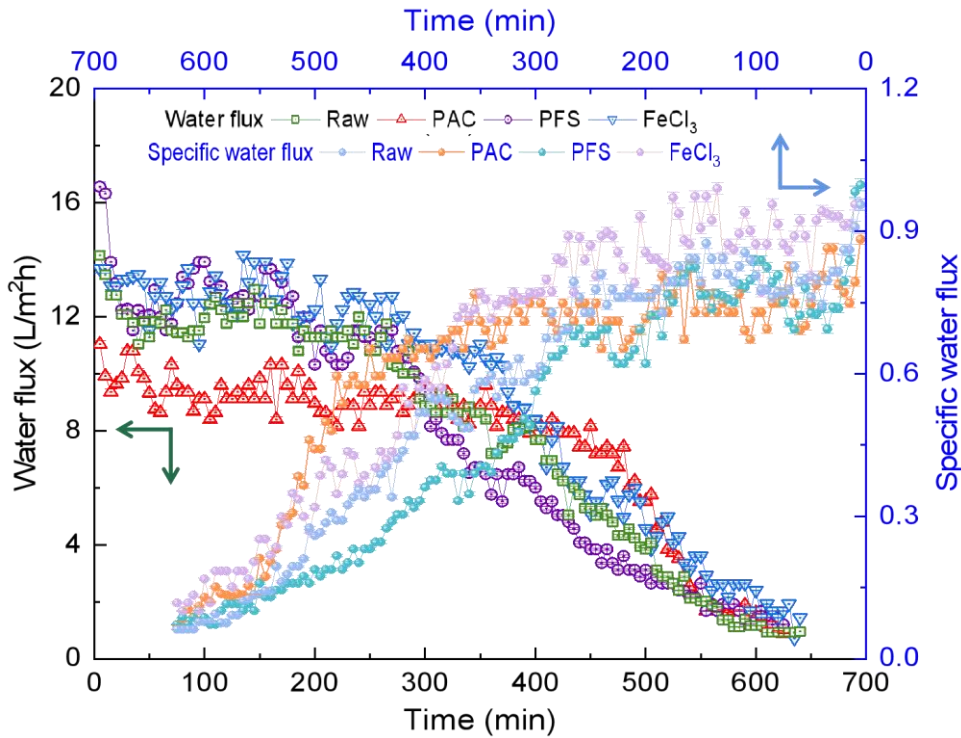
201 Since its more effective complexation with organic substances, FeCl₃ exhibited much
202 higher floc settling ratio to indicate stronger floc formation in comparison to both PAC
203 and PFS (Fig. 2C). This result could be attributed to the dosage of FeCl₃ to induce smaller
204 nano-scale primary particles with more connection points to form strong floc with high
205 setting ratio.²⁸ Furthermore, the floc settling ratio increased notably for all three
206 coagulants in response to an increase in their dosages. Similar results have also been
207 reported previously in potato starch wastewater treatment and could be related to an
208 increase in active sites that could bind to particle surface as the addition of coagulants
209 increased, thereby strengthening particle bridging and adsorption to facilitate floc
210 settlement.²⁹

211 *3.2 Membrane distillation of coagulated leachate concentrate*

212 *3.2.1 Membrane flux*

213 Leachate concentrate before and after coagulation by the three chemicals at the dosage of
214 1200 mg/L was further treated by MD (Fig. 4). The water flux decreased notably in MD
215 operation regardless of raw or coagulated leachate concentrate as the feed solution. This
216 observation was expected as organic substances, such as humic acid, and dissolved
217 inorganic salts in landfill leachate concentrate were further enriched in MD operation for
218 clean water extraction.³⁰ In detail, three stages of flux decline, including notable decrease
219 within the first 50 min, relative stabilization thereafter, and another considerable
220 reduction from 300 min onward, were observed during approximately 650 min of MD
221 operation. Similar results have also been reported previously and could be ascribed to the
222 interaction between foulants and MD membrane surface. It has been reported that humic
223 acid and colloidal particles in the feed solution could rapidly form cake layer, reducing
224 abruptly the water flux in MD operation.³¹ Subsequently, the water flux remained
225 relatively stable, probably due to the deposition of cake layer on the membrane surface to

226 block membrane pore clogging.³² Finally, the water flux declined gradually with the
227 enrichment of organic and inorganic substances in the feed solution, especially humic
228 acid and Ca^{2+} , to intensify the development of cake layer during MD operation.^{29,33}



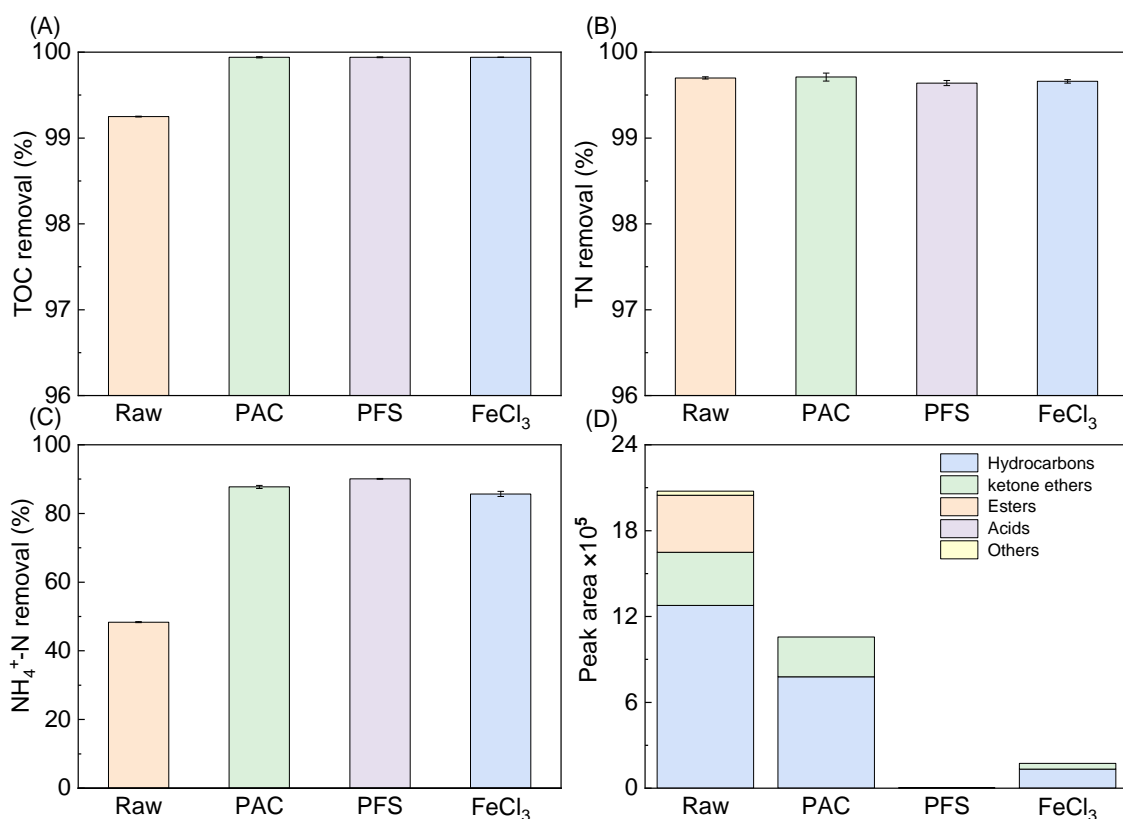
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230 **Fig. 4:** Water flux and specific water flux of MD with raw and coagulated landfill leachate
231 concentrate as the feed solution. PAC, PFS and FeCl_3 were dosed at 1200 mg/L. All MD
232 processes were operated at the cross-flow velocity of 1.7 cm/s with the feed and distillate
233 temperature at 50 ± 1 and 20 ± 1 °C, respectively.

234 Coagulation by the three chemicals resulted in different impacts on MD water flux (Fig.
235 4). Compared to other coagulants, FeCl_3 pretreatment showed the least fouling ($P < 0.05$)
236 given its slightly higher water flux, particularly within the first 400 min of MD operation.
237 This observation could be related to more effective removal of foulants from leachate
238 concentrate, such as humic acid, by FeCl_3 in comparison to other coagulants as discussed
239 above. Nevertheless, such improvement in MD water flux was insignificant thereafter as
240 coagulation was ineffective to remove dissolved salts, such as Mg^{2+} and Ca^{2+} (Fig. S3,
241 Supplementary Data), which could induce membrane scaling and bridge the aggregation
242 of organic substances to aggravate cake layer formation onto membrane surface.¹³ It is

243 noteworthy that the MD water flux after PFS coagulation was comparable to that by FeCl₃
244 pretreatment within the first 300 min, which however, decreased notably to lower than
245 that without coagulation. This lower water flux was possibly due to the lower removal of
246 Mg²⁺ and Ca²⁺ by PFS to exacerbate membrane fouling (Fig. S3, Supplementary Data).
247 By contrast, PAC coagulation reduced the initial MD water flux, particularly within the
248 first 300 min in comparison to that without coagulation pretreatment. This result could be
249 attributed to ineffective floc formation when PAC was added to leachate concentrate for
250 coagulation and the residual of Al³⁺ ions to trigger complexes of aluminum and natural
251 organic matter to facilitate cake layer formation in subsequent MD operation.³⁴

252 ***3.2.2 Removal of bulk organic matter and nutrients***

253 Coagulation pretreatment reduced the concentration of organic matter and nutrients in
254 leachate concentrate and thus enhanced MD performance for their retention (Fig. 5).
255 Compared to raw leachate concentrate, the enhancement in MD retention after
256 coagulation was insignificant for bulk organic substances as indicated by TOC and TN
257 with the rejection rate of > 99% (Fig. 5A&B). TOC in leachate concentrate were mainly
258 contributed by humic substance, which hardly permeated through hydrophobic MD
259 membrane.³⁵ Nevertheless, the retention of NH₄⁺-N by MD increased from approximately
260 50% to higher than 85% after coagulation. This notable increase could be attributed to the
261 hydrolysis of metal ions in coagulants to produce hydrogen ions (H⁺) to reduce the
262 solution pH (Fig. S4, Supplementary Data) for the transformation of free ammonia to
263 NH₄⁺-N to reduce its permeation through the MD membrane.^{13,36} Nevertheless, the
264 dosage of FeCl₃ induced more notable decline in solution pH but lower retention of NH₄⁺-
265 N in comparison to PFS (Fig. S4, Supplementary Data). Such discrepancy could be
266 related to susceptibility of chemical coagulants to solution pH as the abundance of H⁺
267 could restrain Fe hydrolysis to compromise organic coagulation and thus aggregate
268 membrane fouling to enhance NH₄⁺-N transmembrane transportation via severe
269 concentration polarization.³⁷



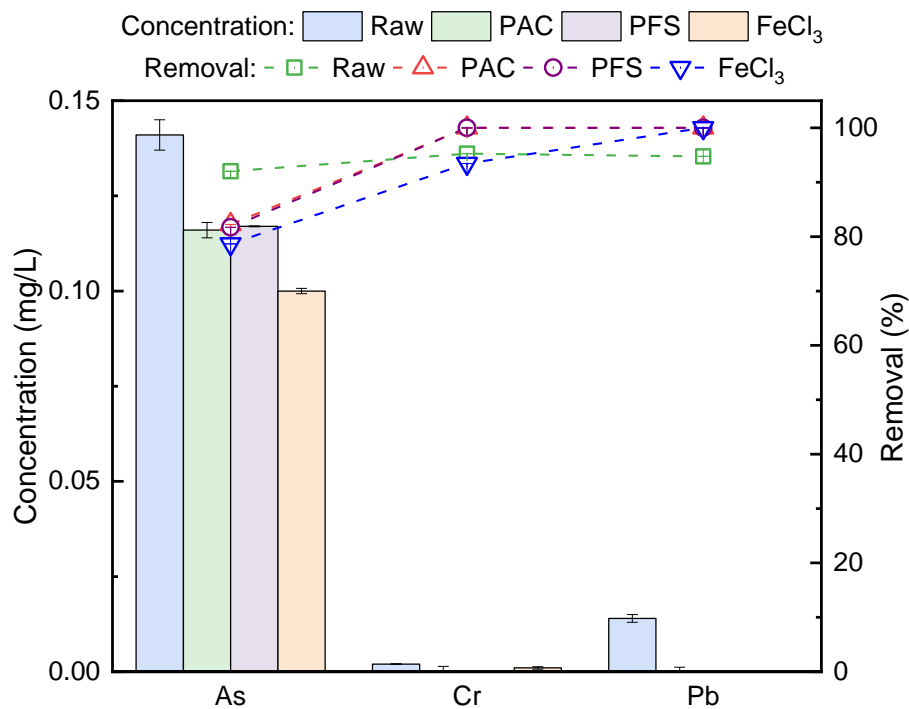
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271 **Fig. 5:** Effect of coagulation on the retention of (A) TOC, (B) TN, and (C) NH₄⁺-N as
 272 well as (D) the concentration of VOCs in distillate during MD operation. Experimental
 273 conditions are shown in the caption of Fig. 4.

274 Coagulation could effectively reduce VOCs in leachate concentrate to mitigate their
 275 permeation through hydrophobic MD membrane (Fig. 5D). Without coagulation
 276 pretreatment, hydrocarbons, ketones and esters were main VOCs to permeate into MD
 277 distillate. Of the three coagulants, PFS could completely alleviate VOCs permeation,
 278 followed by FeCl₃ and PAC. As a polymeric coagulant, PFS could form hydrolysates with
 279 larger molecular weight and higher positive charge than FeCl₃ to induce stronger
 280 adsorption bridging for the removal of VOCs.³⁸ It seems that all three coagulants could
 281 effectively target esters to facilitate its complete removal in subsequent MD operation.
 282 This result could be attributed to the adsorption between the hydrolysates of coagulants
 283 and esters via hydrophobic interaction.³⁹

284 3.2.3 Removal of heavy metals

285 Coagulation pretreatment could enhance the retention of heavy metals by MD and thus
 286 reduced their occurrence in the distillate (Fig. 6). Of the three detected heavy metals, Cr
 287 and Pb could be almost completely retained by MD; while the rejection of As was in the
 288 range of 75 – 95% for either raw or coagulated leachate concentration. The relatively
 289 lower retention of As by MD could be related to volatile organic arsenic, such as
 290 methylated arsenic in the landfill leachate concentrate, to penetrate through the
 291 hydrophobic membrane.⁴⁰ In particular, coagulation by the three chemicals reduced the
 292 rejection of As by MD. This result was unexpected and possibly due to the reduction and
 293 destruction of humic substance by coagulation to prompt the release of As (Fig. S5,
 294 Supplementary Data).⁴¹

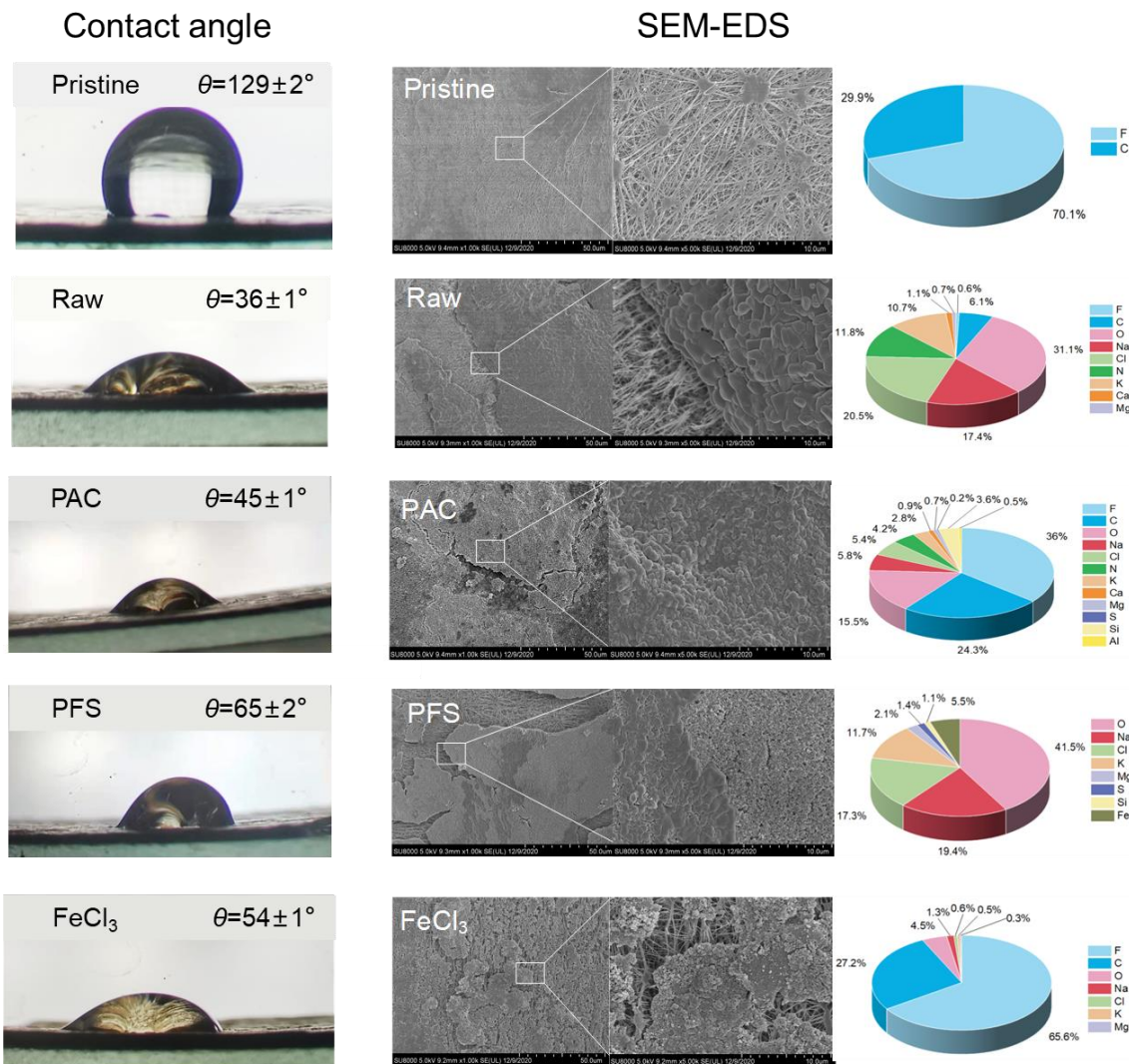


295
 296 **Fig. 6:** Effect of coagulation on the retention of heavy metals by MD and their
 297 concentration in the distillate. Experimental conditions are shown in the caption of Fig.
 298 4.

299 3.3 Membrane fouling layer characterization

300 Membrane morphology and hydrophobicity were monitored to decipher the fouling
 301 behavior of MD. The SEM images showed that coagulation pretreatment could mitigate

302 cake layer formation on the membrane surface (Fig. 7). The pristine membrane exhibited
303 a smooth and filamentous surface, which however, was completely covered by a thick
304 cake layer with the aggregation of large molecular particles in the MD treatment of raw
305 leachate concentrate (Fig. 7A). By contrast, coagulation pretreatment led to the dispersion
306 of cake layer on the membrane surface with more dense structure in MD operation,
307 particularly for PAC. As such, no significant increase or even a reduction in MD water
308 flux was observed in the treatment of coagulated leachate concentrate as discussed above
309 (Fig. 4). Compared to PAC and PFS, the cake layer seemed to be fluffier to faintly expose
310 the filamentous structure of raw membrane after FeCl_3 coagulation of leachate
311 concentrate (Fig. 7E). Further element analysis of the cake layer by EDS identified C
312 (6.1%-27.2%), O (4.5%-38.6%), Na (1.3%-18.1%), Mg (0.3%-2.0%) and inorganic ions
313 from coagulants, such as Al (0.5%), Cl (0.6%-20.5%) and Fe (5.1%) (Fig. 7 & Table S1,
314 Supplementary Data), to indicate the composition of both organic and inorganic
315 foulants.¹⁴

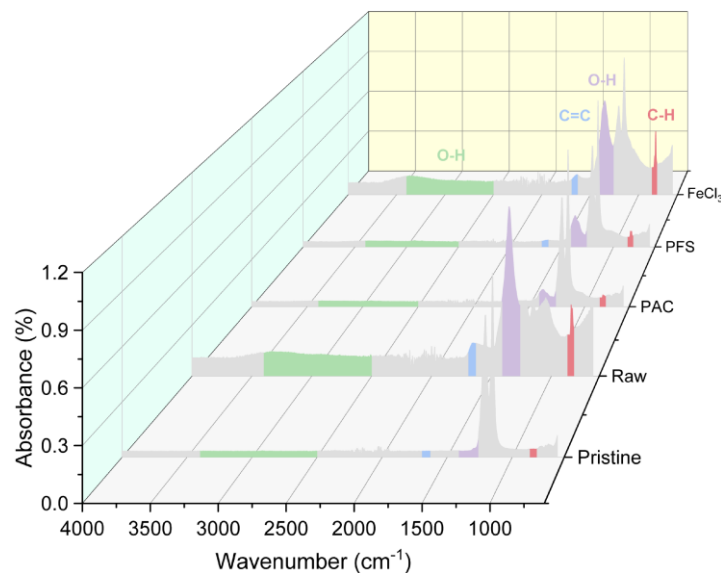


316

317 **Fig. 7:** Contact angle and SEM-EDS measurements of pristine and fouled membrane after
 318 MD operation for landfill leachate concentrate treatment. Experimental conditions are
 319 shown in the caption of Fig. 4.

320 Coagulation pretreatment could alleviate the coverage of thick cake layer and the
 321 reduction of membrane hydrophobicity as indicated by contact angle in leachate
 322 concentrate treatment (Fig. 7). Of the three coagulants, PFS pretreatment contributed to
 323 the highest contact angle (65°), followed by FeCl₃ (54°) and PAC (45°), respectively. This
 324 result could be attributed to more dense deposition of hydrophobic organic matter on the
 325 membrane surface via hydrophobic-hydrophobic and electrostatic interaction.^{31,42,43} As
 326 such, MD was more effective to retain organic matter and NH₄⁺-N when PFS was used
 327 for leachate concentrate coagulation in comparison to other two chemicals (Fig. 5).

328 The functional groups onto membrane surface were characterized by FTIR. As shown in
329 Fig. 8, the ATR-FTIR spectra demonstrated that the fouled membrane surface exhibited
330 notable adsorption peaks at 810 – 865 cm^{-1} , which were usually associated with bending
331 vibration of C-H in aromatic compounds, at 1260 and 1410 cm^{-1} , representing bending
332 vibration of O-H in phenols and alcohols, and at 1633 cm^{-1} to indicate the stretching
333 vibration of C=C in olefins, in comparison to the pristine membrane. Moreover, the large
334 wavenumber band between 2500 and 3400 cm^{-1} associated with O-H was observed for
335 all fouled membranes to indicate the occurrence of hydrogen bonds.⁴⁴ Compared to raw
336 leachate concentrate, its coagulation by the three chemicals could effectively remove
337 organic matter, particularly humic substance, thereby declining the peaks of functional
338 groups and thus organic affinity on MD membrane surface. It is noteworthy that PAC
339 coagulation resulted in lower peak areas of functional groups on membrane surface (Fig.
340 8), but more notable flux decline within the first 300 min during MD operation in
341 comparison to other two coagulants (Fig. 4). This result was possibly due to the high
342 contents of Mg^{2+} and Ca^{2+} in leachate concentrate after PAC coagulation to induce severe
343 membrane scaling (Fig. S3, Supplementary Data).



344
345 **Fig. 8:** FTIR spectra of pristine and fouled membrane after MD operation for landfill
346 leachate concentrate treatment. Experimental conditions were as shown in the caption of
347 Fig. 4.

348 **4 Conclusion**

349 Results reported here show that coagulation could effectively remove organic matter from
350 landfill leachate concentration to improve its subsequent treatment by MD with enhanced
351 contaminant retention and mitigated membrane fouling. FeCl₃ exhibited the highest
352 removal of organic matter in landfill leachate concentrate than PFS and PAC at their
353 optimal dosage of 1200 mg/L as indicated by both TOC and TN reduction. The
354 coagulation by all these chemicals enhanced the retention of organic matter and
355 contaminants by MD. In particular, NH₄⁺-N retention by MD was increased from 48.3%
356 to 90.1% after coagulation of landfill leachate concentrate. Furthermore, heavy metals
357 and VOCs could be highly retained by MD, especially when PFS was used as the
358 coagulant. Moreover, PFS was more effective to mitigate MD membrane fouling by
359 reducing the occurrence of both organic and inorganic foulants (e.g. humic acid, Ca²⁺,
360 and Mg²⁺) in the leachate concentrate in comparison other two coagulants.

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364 Development Program of China Agricultural University, and the Project of Science and
365 Technology Administration of Sanya Yazhou Bay, China (SYND-2021-09).

366 **References**

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