

1 ***Moringa oleifera* coagulation as pretreatment prior to microfiltration for**  
2 **membrane fouling mitigation**

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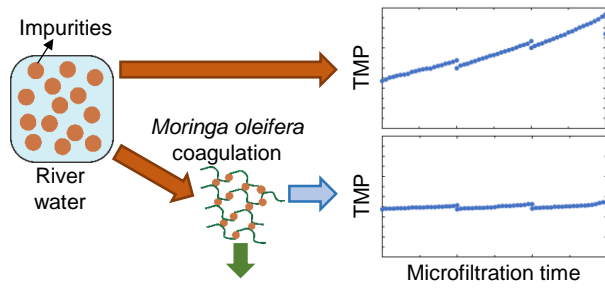
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15 **TOC contents**



16

17 Coagulation pretreatment using *Moringa oleifera* in microfiltration of a river water achieved

18 membrane fouling mitigation and filtered water quality improvement.

19 **Abstract**

20 Coagulation using *Moringa oleifera* (MO), a natural coagulant, is an attractive approach in  
21 drinking water treatment to break away from conventional chemical coagulation using  
22 aluminium or iron salts. This study aimed to evaluate the effect of pre-filtered MO coagulation  
23 pretreatment on the fouling mitigation in microfiltration (MF) process. MF treatment of a river  
24 water without pretreatment promoted a considerable reduction in membrane permeability (i.e.  
25 membrane fouling), which was not sufficiently recovered by conventional backwashing. In  
26 contrast, MF treatment after MO coagulation substantially reduced membrane fouling. Over six  
27 filtration cycles (or 6 h filtration period), the fouling mitigation level with MO coagulation was  
28 comparable to that with aluminium sulphate (alum) coagulation. In addition, major water quality  
29 (turbidity and colour) after MF treatment was equivalent between MO and alum coagulation.  
30 Pretreatment by MO coagulation has an advantage of maintaining water pH after MF treatment.  
31 The results obtained here suggest that MO coagulation can be employed as an effective and low-  
32 cost fouling mitigation technique for MF process in drinking water treatment.

## 33 **1. Introduction**

34 There is a growing interest in *Moringa oleifera* (MO) seed as an alternative to chemical  
35 coagulants such as aluminium sulphate (alum) and ferric chloride in recent years.<sup>1,2</sup> In a typical  
36 drinking water treatment, coagulation followed by sedimentation and sand filtration plays an  
37 important role in removing particulate matter.<sup>3</sup> MO seeds contain dimeric cationic proteins,<sup>4</sup>  
38 which can be extracted from MO seeds using water or salt solution and used for coagulation  
39 applications.<sup>5</sup> MO coagulation is based on the net-like structure coagulation mechanism, that is  
40 effective for turbidity removal.<sup>5</sup> For example, previous studies<sup>6-8</sup> demonstrated that MO  
41 coagulation achieved from 60% to almost complete removal of turbidity for high turbid surface  
42 waters with 50–450 NTU. MO is not toxic; thus, even when coagulation is not correctly  
43 performed causing overdosing, no adverse effects on public health are expected in case of  
44 overdosing. In addition, given its organic nature, coagulant sludge generated through MO  
45 coagulation can be processed for use as animal feed or plant fertilizer.<sup>9</sup> MO is a fast growing  
46 tree, commonly found in semiarid, tropical and sub-tropical areas including India, South and  
47 Central America, Africa and South East Asia.<sup>10</sup> Thus, MO coagulation is a pragmatic option to  
48 provide access to safe drinking water to rural communities in developing countries around the  
49 world as stated in the Millennium Development Goals by the United Nation.

50 Gravity driven membrane filtration is another technology that has significantly improved access  
51 to safe drinking water.<sup>11</sup> Notable examples include the Skyjuice<sup>12</sup> and Aqua CUBE systems, in  
52 which water is driven through a microfiltration (MF) by gravity. MF has been widely used for  
53 drinking water treatment to reliably remove suspended solids and pathogens such as protozoa  
54 and pathogenic bacteria.<sup>13,14</sup> A major challenge in using MF for low cost drinking decentralised

55 water treatment is membrane fouling, which is caused by the deposition of colloidal and organic  
56 substances on the membrane surface or in the membrane pores and can reduce membrane  
57 permeability and separation performance.<sup>15-17</sup> Membrane fouling in MF can be controlled by  
58 frequent backwashing or chemical cleaning. However, these methods are not compatible with  
59 decentralised water treatment. A more suitable approach is to apply pre-coagulation prior to MF  
60 treatment.<sup>18</sup>

61 The effectiveness of coagulation pretreatment with alum or ferric chloride to mitigate MF  
62 membrane fouling has been demonstrated in the literature.<sup>19, 20</sup> The reduced membrane fouling  
63 can be attributed to coagulation process capable of removing suspended solids and dissolved  
64 organic matter.<sup>21</sup> Although alum and ferric coagulation have been successfully used as a  
65 membrane fouling mitigation technique in drinking water treatment, the use of these heavy metal  
66 coagulants may be inappropriate in some developing countries due to the unaffordable high costs  
67 of imported chemicals<sup>6</sup> and MO coagulation can be an alternative pretreatment. In fact, previous  
68 studies have successfully applied MO coagulation to pretreat high turbidity (>500 NTU) waters  
69 such as dairy wastewater<sup>22, 23</sup> and secondary oxidation pond effluent<sup>24</sup> prior to MF operation. MO  
70 coagulation pretreatment can possibly substitute backwashing to reduce the complexity of MF  
71 operation in drinking water applications, making it more amendable to small rural communities.  
72 However, when a low turbidity water (such as river water) was used as the feed, MO coagulation  
73 could only achieve about 60% turbidity removal.<sup>2</sup> Moreover, since it is an organic based  
74 coagulant, MO coagulation prior to MF filtration can result in the considerable increase in  
75 organic matter concentration in the pretreated water.<sup>25</sup> Previous studies<sup>26, 27</sup> have identified that  
76 an improvement in the extraction method of MO coagulant can be attained through pre-filtration

77 of MO seed powder. To date, the pre-filtered MO coagulant has not been applied to the  
78 pretreatment of membrane filtration.

79 This study aimed to evaluate the effects of pre-filtered MO coagulation on the fouling mitigation  
80 of MF treatment in drinking water applications. MO dose in a surface water with low turbidity  
81 was optimised for turbidity removal and fouling mitigation. Thereafter, MO coagulation on the  
82 fouling mitigation of MF treatment was evaluated over six filtration cycles, and the results were  
83 compared with that of alum coagulation. This study also examined water quality after  
84 coagulation followed by MF treatment.

## 85 **2. Materials and methods**

### 86 **2.1 Chemicals**

87 Analytical grade alum ( $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ ) and sodium chloride (NaCl) were purchased from  
88 Wako Pure Chemical Industries (Tokyo, Japan). A stock solution of alum coagulant was  
89 prepared in Milli-Q water to obtain 1000 mg-Al/L. A NaCl solution of 1 M was also prepared in  
90 Milli-Q water and used for MO coagulant extraction. Tap water was treated using a reverse  
91 osmosis system and used for backwashing water. River from Nagasaki, Japan was used to  
92 present surface water. The river water collected in December was stored at 4 °C and was used  
93 within one week.

### 94 **2.2 MO coagulant**

95 MO seeds were collected from Tamil Nadu, India. The MO seeds were first ground into powder.  
96 Then 1 g of MO powder was dissolved with 100 mL Milli-Q water at 30 °C. Thereafter, the

97 obtained MO solution was stirred for 5 min and allowed to settle for 10 min. The supernatant of  
98 MO solution was filtered with a 0.45  $\mu\text{m}$  filter (Thermo Scientific, Waltham, NA, USA) and the  
99 filtrate was discarded. Solid residue on the filter was washed by 100 mL of 1 M NaCl. The  
100 obtained solution was filtered again via the same protocol described above (i.e. stirred for 5 min,  
101 settled for 10 min, and filtered to obtain 100 mL of clear filtrate). The final filtrate was used as  
102 MO coagulant for subsequent experiments.

### 103 **2.3 Membrane module and filtration system**

104 A hollow fibre polyvinylidene fluoride (PVDF) MF membrane with nominal pore size of 0.1  $\mu\text{m}$   
105 (Microza<sup>®</sup> USP-043, Asahi Kasei, Tokyo, Japan) was used in this study. The MF membrane was  
106 supplied in a module with length of 132 mm, external diameter of 1.4 mm, internal diameter of  
107 0.7 mm and effective membrane area of 120  $\text{cm}^2$ . The membrane module is designed to operate  
108 in the inside-out filtration orientation. The module is integrated into a laboratory-scale dead-end  
109 filtration system comprising 2 L glass feed reservoir, flow meter, a peristaltic pump for filtration  
110 (Kros Flo<sup>®</sup> Research pump, Spectrum Laboratories, CA, USA), a peristaltic pump for  
111 backwashing (Q-100, Tacmina, Osaka, Japan), a temperature control unit (ACE-2000, Tokyo  
112 Rikakikai, Tokyo, Japan), valves and pressure gauges (**Fig. S1**).

### 113 **2.4 Experimental protocols**

#### 114 **2.4.1 Coagulation experiment**

115 Coagulation experiments were performed using a jar test system (JMD-3E, Miyamoto Riken  
116 Industry, Osaka, Japan). This jar test system was equipped with a series of 1 L beakers and  
117 stirring shafts. The stirring speed of these shafts can be changed automatically. Each beaker was

118 filled with 1 L of river water. Immediately after coagulant addition, the beakers were rapidly  
119 mixed for 2 min at 150 rpm. The coagulant dose was from 0 to 8 mL-MO/L and 0 to 10 mg-Al/L  
120 for MO and alum, respectively. After rapid mixing, the water was flocculated for 30 min at a  
121 mixing speed of 30 rpm. Then, the beakers were left undisturbed for sedimentation for 1 h. The  
122 supernatant was then collected for subsequent filtration experiments and water quality analysis.

### 123 **2.4.2 MF treatment**

124 Prior to each MF filtration experiment, integrity of the membrane module was confirmed by  
125 measuring the clean water permeability at 20 °C. Thereafter, the feed reservoir was filled with a  
126 river water (a) without pre-treatment, (b) after MO coagulation or (c) after alum coagulation.  
127 Each filtration cycle comprised of two steps: filtration and backwashing. Filtration was  
128 conducted at the permeate flux of 140 L/m<sup>2</sup>h (at 20 °C) for 1 h. Membrane fouling was  
129 monitored by the transmembrane pressure (TMP). At the end of the filtration step, backwashing  
130 was applied using clean water at the flux of 280 L/m<sup>2</sup>h (at 20 °C) for 1 min. The next filtration  
131 cycle was then repeated as described above. After each experiment, chemical cleaning was used  
132 to restore the membrane permeability to within 1% the initial value. Chemical cleaning was  
133 conducted by soaking the membrane overnight in 1% sodium hydroxide and 400 ppm of sodium  
134 hypochlorite at room temperature. The membrane was then rinsed with a copious amount of  
135 clean water to remove any residual chemicals.

### 136 **2.5 Analytical techniques**

137 The water quality parameters analysed here include turbidity, colour, pH, electrical conductivity  
138 and total organic carbon (TOC). Turbidity and colour measurements were conducted using water  
139 analyser turbidity meter (WA1, Nippon Denshoku, Tokyo, Japan). The pH was measured using a



140 pH meter (SK-620 PH II, Sato, Tokyo, Japan). Electrical conductivity was measured using a  
141 conductivity meter (AS 710, As One Corporation, Shanghai, China). TOC was measured using a  
142 total organic analyser (TOC-VCSD, Shimadzu, Kyoto, Japan). Zeta potential of substances in  
143 water was analysed using a rectangular micro-electrophoresis cell (ZEECOM ZC-2000, Microtec  
144 Co., Funabashi, Japan). The zeta potential of 30 particles was measured and averaged in this  
145 study. Size distribution of particles over 100 nm (equivalent to membrane pore size) in water  
146 samples was measured using NanoSight LM10 (Malvern Panalytical, Malvern, UK), which  
147 utilizes light scattering and Brownian motion for the characterization of nanometer size particles.

## 148 **2.6 Fouling model description**

149 Membrane fouling in constant flow of MF typically progresses following one of the following  
150 models: complete blocking, standard blocking, intermediate blocking, or cake filtration models.  
151 In general, pore blocking occur immediately after the start of filtration, which is followed by  
152 cake filtration.<sup>28,29</sup> These four modes of fouling can be expressed as follows:<sup>30</sup>

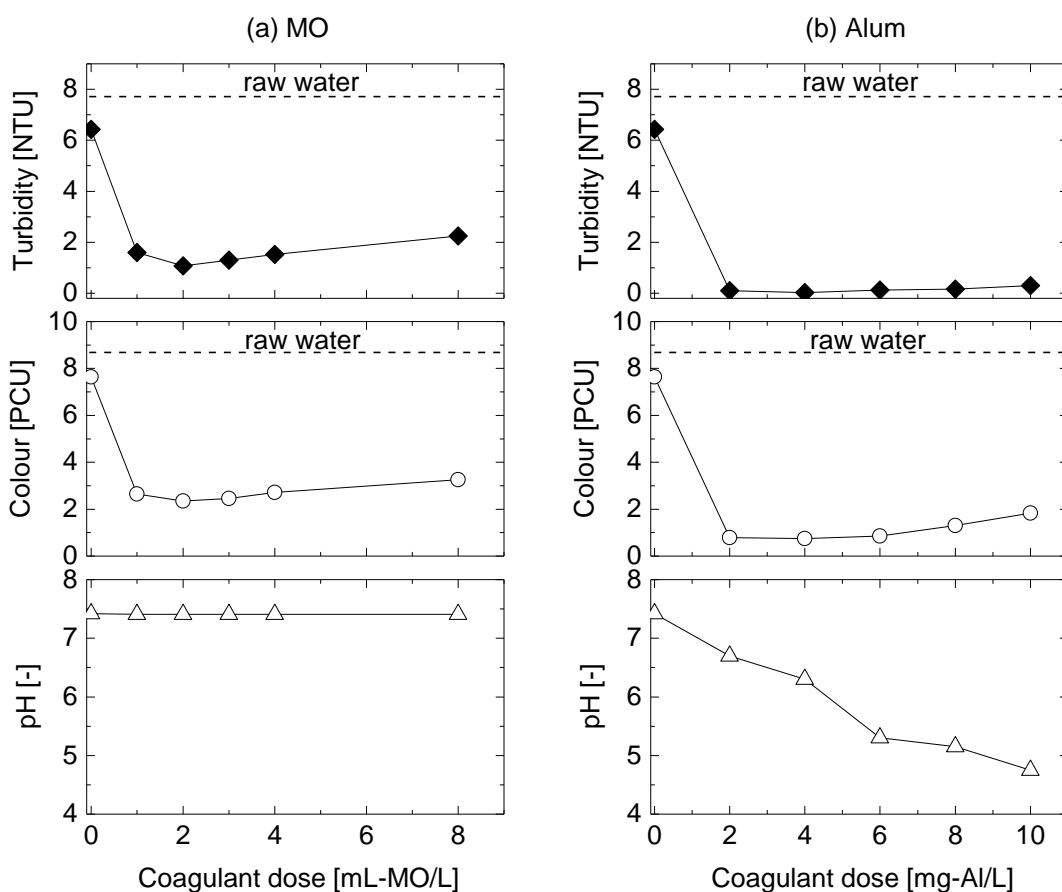
$$153 \quad \frac{dP_t}{dt} = k(\Delta P_t)^n \quad (1)$$

154 where  $t$  = filtration time [min],  $P_t$  = transmembrane pressure [kPa] at filtration time  $t$ ,  $k$  = a  
155 constant of the fouling law, and  $n$  = the fouling index. Predominant fouling mechanisms (i.e.  
156 complete blocking, standard blocking, intermediate blocking, or cake filtration) can be  
157 determined based on the fouling index ( $n$ ) (2.0, 1.5, 1.0, and 0, respectively).<sup>30</sup> This study used  
158 the pressure data collected every 6 min was used for the calculation.

### 159 3. Results and discussion

#### 160 3.1 Coagulation

161 Coagulant doses of MO and alum coagulants were optimised based on the removal of turbidity  
162 and colour. The optimum coagulant doses of MO and alum were at 2 mL-MO/L and 4 mg-Al/L,  
163 respectively (**Fig. 1**). MO coagulation reduced turbidity and colour from 7.8 to 1.1 NTU and  
164 from 8.7 to 2.4 PCU, respectively. Alum coagulation resulted in better turbidity and colour  
165 removal, achieving 0.1 NTU and 0.8 PCU after coagulation, respectively. The optimum turbidity  
166 removal by alum was 99.7%, which was considerably better than that by MO (86%). Similarly,  
167 alum coagulation resulted in 91% colour removal, which was higher than MO coagulation (72%)  
168 (**Fig. 1**). Lower turbidity and colour removal efficiencies by MO coagulant can be explained by  
169 their lighter and smaller flocs compared to those from alum. MO flocs had poor settleability as  
170 previously reported by Okuofu.<sup>31</sup> For both MO and alum, increasing the coagulant dose beyond  
171 the optimum value resulted in increased residual turbidity and colour. Over-dose of MO can  
172 cause the saturation of the polymer bridge sites and increased charge repulsion due to MO's  
173 cationic poly-electrolyte.<sup>8</sup> These phenomena can destabilize colloids and particles, inhibiting the  
174 removal of turbidity. Results in **Fig. 1** indicate that MO coagulant dose needs to be precisely  
175 regulated to optimise turbidity removal.



176  
 177 **Fig. 1** – Removal of turbidity and colour, and change in pH in the surface water at various  
 178 coagulant doses of (a) MO and (b) alum.

179 In terms of other major water quality parameters, solution pH was not affected by MO  
 180 coagulation at 0–8 mL-MO/L dose (**Fig. 1**). In contrast, alum coagulation resulted in a  
 181 considerably drop in the water pH from 7.4 (initial surface water) to 6.3 when the alum dose  
 182 increased to 4 mg-Al/L. On the other hand, a small but discernible increase in conductivity was  
 183 observed from 270 to 286  $\mu\text{S}/\text{cm}$  at the optimum MO dose (**Table 1**). The increase in  
 184 conductivity can be ascribed to the addition of NaCl used for extracting MO coagulation as  
 185 described in section 2.2. In addition to conductivity, MO coagulation resulted in a slight increase  
 186 in TOC concentration, from 15.3 to 15.7 mg/L at the optimum dose. An increase in the

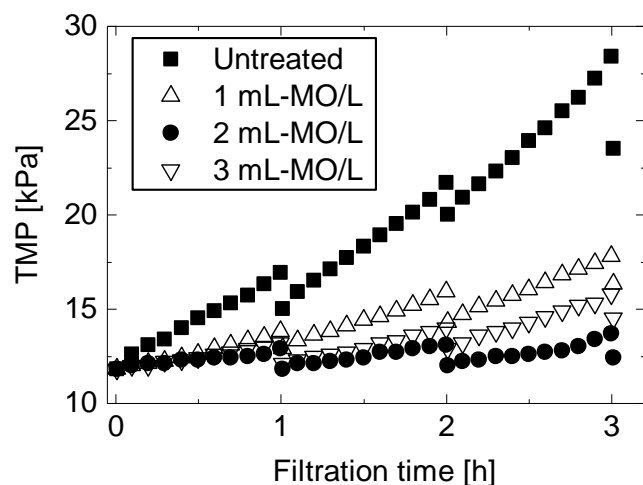
187 concentration of organic matter in treated water is one of the major drawbacks of MO.<sup>8, 9, 32</sup> In  
 188 contrast, alum coagulation could achieve about 8% TOC removal (**Table 1**). The reduction in  
 189 TOC concentration in alum coagulation is mainly due to adsorption and complexation with  
 190 positively charged aluminium ions under acidic conditions, forming insoluble particulate  
 191 aggregates.<sup>33</sup>

192 **Table 1** – Water quality before and after coagulation at their optimum doses (2 mL-MO/L and 4  
 193 mg-Al/L).

Parameter	Untreated water	MO-treated water	Alum-treated water
Turbidity (NTU)	7.8	1.1	0.1
Colour (PCU)	8.7	2.4	0.8
Conductivity ( $\mu\text{S}/\text{cm}$ )	270	286	351
TOC (mg/L)	15.3	15.7	14.0
pH	7.4	7.4	6.3

194 **3.2 Optimisation of coagulant dose for fouling mitigation**

195 Results from MO optimisation experiments were used to evaluate the performance of MO  
 196 coagulation pretreatment to mitigate MF membrane fouling. MF treatment of the river water  
 197 without pretreatment resulted in a rapid increase in TMP from 12 to 17 kPa within the first  
 198 filtration cycle (0–60 min) (**Fig. 2**). Moreover, backwashing with clean water was not capable of  
 199 restoring membrane permeability. As a result, after three filtration cycles TMP reached 24 kPa,  
 200 twice higher than the initial TMP.



201

202 **Fig. 2** – TMP increase in MF treatment of waters treated with MO coagulant (permeate flux =

203 140 L/m<sup>2</sup>h, backwashing flux = 280 L/m<sup>2</sup>h and backwashing time = 1 min).

204 MO coagulation performed prior to MF effectively reduced membrane fouling at all MO doses

205 selected here (1, 2 and 3 mL-MO/L), which correspond to residual turbidity removals of 75%,

206 86% and 83%, respectively. The significant reduction in membrane fouling by MO coagulation

207 is due likely to the improved transformation and removal efficiency of colloids from water prior

208 to MF treatment. During the coagulation and sedimentation processes, aggregation of small

209 colloids and dissolved matter can lead to a larger and effective particle size, which can result in

210 less specific membrane resistance.<sup>34</sup> In addition, organic matter and colloidal particles

211 transformed into flocs can easily be removed by backwashing.<sup>35</sup> The results revealed that the

212 effect of fouling mitigation by MO coagulation can be maximized at 2 mL-MO/L dose, which

213 resulted in only an increased TMP from 12.0 to 12.4 kPa over three filtration cycles (**Fig. 2**). In

214 contrast, 3 mL-MO/L appeared to be an overdose, resulting in a discernible increase in TMP

215 from 12 to 15 kPa in three filtration cycles. Likewise, a lower dose at 1 mL-MO/L was not

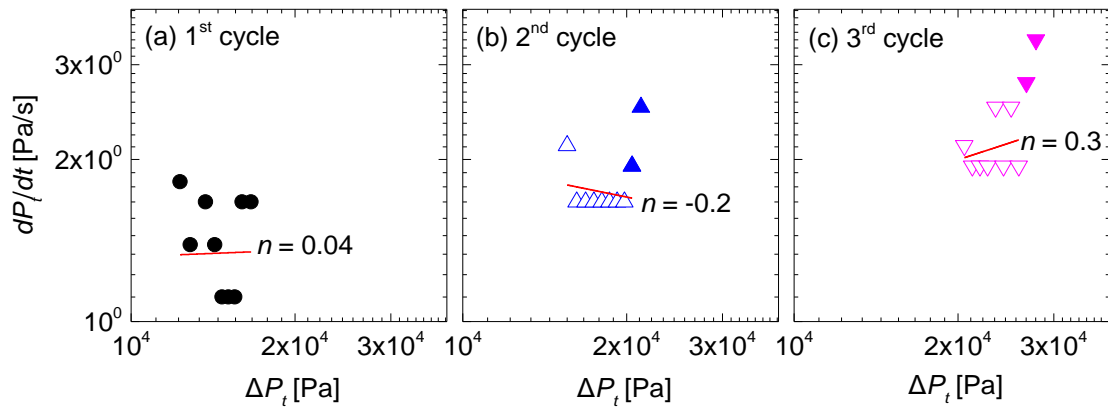
216 sufficient to effectively mitigate membrane fouling. The results here indicate that the MO dose

217 optimised for turbidity removal can be an important control parameter for membrane fouling

218 mitigation in MF process. Therefore, monitoring turbidity in MF feed (i.e. coagulation effluent)  
219 can be an operating parameter to maintain the minimum level of membrane fouling.

220 Membrane fouling during MF treatment without pretreatment was further analyzed using the  
221 filtration model that can differentiate three pore blocking and one cake filtration mechanisms. It  
222 is noted that the results during MF treatment with MO coagulation could not be analyzed using  
223 the filtration model, because the TMP increase was too small for an accurate model fitting.

224 Overall, membrane fouling during MF treatment progressed following the cake layer filtration  
225 mechanism. The slope ( $n$ ) calculated based on the data during the all filtration cycles were close  
226 to zero ( $n = -0.2-0.3$ ) when the last twelve minutes data of 2<sup>nd</sup> and 3<sup>rd</sup> filtration cycle was  
227 excluded (**Fig. 3**). Nevertheless, during the last twelve minutes of the 2<sup>nd</sup> and 3<sup>rd</sup> filtration cycle,  
228 the slope ( $n$ ) increased considerably ( $n = 5-7$ ), which was far beyond the slope range of the  
229 filtration model. These sudden increases may have occurred through the compression of the cake  
230 layer, which could be induced by high feed pressure according to the progress of membrane  
231 fouling.<sup>36-38</sup> The compressed cake layer on the membrane surface can cause more packed fouling  
232 structure, which can increase the significant increase in hydraulic resistance to permeating water.  
233 Overall, the results here suggest that MO coagulation can effectively reduce foulants that form  
234 cake layer on the membrane surface and act as hydraulic resistance.

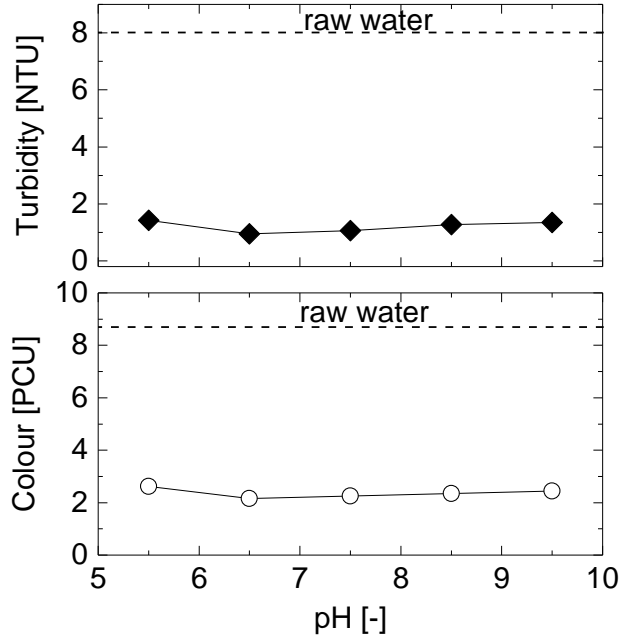


235

236 **Fig. 3** – The derivatives  $dP_t/dt$  as a function of TMP during MF treatment without pretreatment.  
 237 The last 12 minute data in the 2<sup>nd</sup> and 3<sup>rd</sup> cycle was presented in solid symbol.

### 238 3.3 Optimisation of water pH for fouling mitigation

239 The impact of water pH on the removal of turbidity and colour by MO coagulant was evaluated  
 240 at the optimum MO coagulant dose (2 mL-MO/L). As reported in section 3.1, MO coagulant did  
 241 not alter water pH, thus water pH was adjusted prior to coagulation. As a result, negligible  
 242 impact was identified throughout the tested pH (5.5–9.5) (**Fig. 4**). A similar observation with  
 243 negligible impact of water pH on turbidity removal by MO coagulation has been reported in a  
 244 previous literature.<sup>39</sup> MO coagulant in water at the tested pH is positively charged due to the  
 245 isoelectric pH of the cationic proteins at 10.<sup>8</sup> Because colloidal particles in natural water are  
 246 usually negatively charged, the dominant mechanisms of coagulant of charge neutralisation and  
 247 adsorption effects<sup>10</sup> can effectively occur at the experiment pH value. This is a notable advantage  
 248 over alum, which often requires pH adjustment for successful coagulation. A slightly high  
 249 residual turbidity and colour was observed at the lowest pH (5.5). This may be due to the  
 250 increased positive charge of the MO coagulant and reduced negative charge of particles in water.

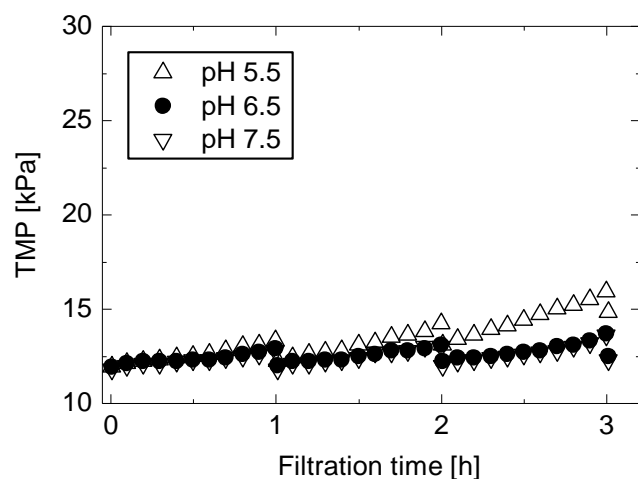


251

252 **Fig. 4** – Removal of turbidity and colour by optimum MO coagulant dose (2 mL-MO/L) at  
 253 variable water pH in the surface water. Optimisation of MO coagulant dose for the specific river  
 254 water is provided in **Fig. S2**.

255 The waters treated by MO coagulation at three pH (5.5, 6.5 and 7.5) were used to evaluate the  
 256 impact of MO coagulation pH on MF membrane fouling. Over the three filtration cycles, a  
 257 negligible difference was observed for pH 6.5 and 7.5 (**Fig. 5**). Coagulation using a surface water  
 258 is typically performed within the pH range. A slightly higher TMP was observed for pH 5.5,  
 259 which is in line with the results for turbidity removal. This indicates that turbidity removal by  
 260 MO coagulation is a key for achieving the optimum effect of membrane fouling mitigation.  
 261 Overall, the results indicate that pH adjustment prior to MO coagulant is not necessary to achieve  
 262 the optimum coagulation and fouling mitigation.





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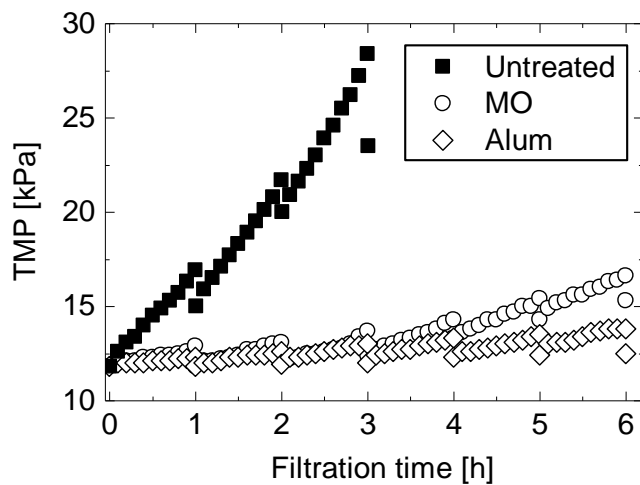
264 **Fig. 5** – Effect of water pH in MF treatment of waters treated with the optimum MO coagulant  
 265 dose of 2 mL-MO/L (permeate flux = 140 L/m<sup>2</sup>h, backwashing flux = 280 L/m<sup>2</sup>h and  
 266 backwashing time = 1 min).

### 267 3.4 Comparison with alum coagulation

#### 268 3.4.1 Membrane fouling

269 To demonstrate the potential of MO as an alternative coagulant of alum for MF treatment, the  
 270 effect of pretreatment on fouling mitigation between MO (2 mL-MO/L) and alum (4 mg-Al/L)  
 271 coagulation was compared. For both coagulants, minor fouling development was observed  
 272 during filtration (**Fig. 6**). MF treatment of the MO-treated river water revealed an increase in  
 273 TMP from 12 to 15 kPa over six filtration cycles. In contrast, alum coagulation prior to MF  
 274 treatment resulted in a less increase in TMP from 12 to 13 kPa. Despite of the relatively large  
 275 difference in residual turbidity between the two coagulants (MO = 1.1 NTU and alum = 0.1  
 276 NTU), they effectively mitigated membrane fouling and the subsequent increase in TMP after six  
 277 filtration cycles was comparable between MO and alum (TMP = 15 and 13 kPa, respectively).  
 278 This was also confirmed in a separate test (**Fig. S3**). These results indicate that sufficient level of

279 membrane fouling mitigation in MF can be achieved through MO coagulation. In addition, the  
280 results suggest that MO is a good alternative to alum and other conventional chemical coagulants  
281 for coagulation pre-treatment prior to MF. Further improvement for membrane fouling  
282 mitigation by MO coagulation can be expected by further optimising coagulation or filtration  
283 conditions. Coagulation condition includes water pH, and filtration conditions include permeate  
284 flux and frequency of backwashing. In addition, modification on the extraction method of MO  
285 coagulant from seeds may improve coagulation performance in terms of turbidity removal,  
286 which can enhance membrane fouling mitigation. However, these further optimisations are  
287 beyond the scope of this study and will be addressed in the future study.

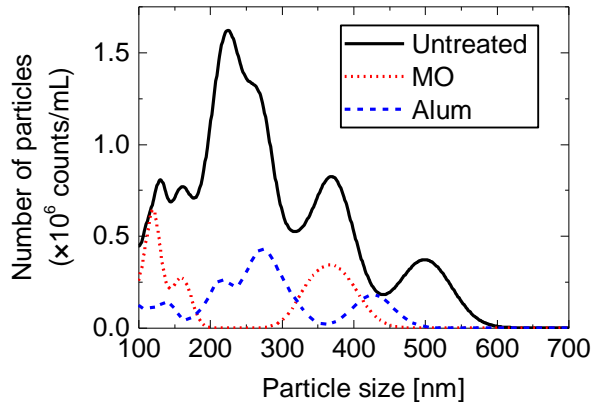


288  
289 **Fig. 6** – Fouling development in MF treatment without pretreatment, with MO coagulation at 2  
290 mL-MO/L or with alum coagulation at 4 mg-Al/L (permeate flux = 140 L/m<sup>2</sup>h, backwashing flux  
291 = 280 L/m<sup>2</sup>h and backwashing time = 1 min).

292 To provide further understanding in the difference of fouling mitigation level between MO and  
293 alum coagulation, zeta potential of suspended particles before and after coagulation treatment  
294 with MO and alum was determined. Zeta potential of suspended particles changed  $-10 \pm 2.9$  mV

295 (untreated water) to  $+0.5 \pm 5.2$  mV (after alum coagulation) and  $-17.0 \pm 5.8$  mV (after MO  
296 coagulation). In other words, alum coagulation resulted in the neutralization of residual  
297 suspended particles while MO coagulation rendered residual suspended particles even more  
298 negatively charged. PVDF membranes are also negatively charged at environmental pH (pH  
299  $\sim 6$ )<sup>13</sup>. Thus, charge neutralization of suspended particles by alum coagulation is expected to  
300 exacerbate membrane fouling. In contrast, electrostatic repulsion between negatively charged  
301 suspended particles after MO coagulation and the negatively charged MF membrane surface can  
302 reduce membrane fouling. However, alum coagulation resulted in slightly better fouling  
303 mitigation than MO coagulation (**Fig. 6**). Thus, it is possible that the contribution of electrostatic  
304 repulsion was small to alleviate fouling was small in comparison with the contribution from  
305 residual organic substances dissolved in water.

306 Additional analysis of particle size distribution revealed that both MO and alum coagulation  
307 were effective to remove suspended particles in the range of 100–600 nm in size (**Fig. 7**).  
308 Compared to MO coagulation, alum coagulation could remove suspended particles in the range  
309 of 100–180 and 320–420 nm more effectively than those in the range of 180–320 nm.  
310 Nevertheless, further research is necessary to clarify the contribution of each size fraction to  
311 membrane fouling. Considering that cake layer is the dominant mechanism of membrane fouling  
312 without coagulation, the reduction in the number of particles over 200 nm (nominal pore size of  
313 the membrane) was expected to play a role in mitigation membrane fouling through alum or MO  
314 coagulation.



315

316 **Fig. 7** – Particle size distribution of waters without pretreatment, with MO coagulation or with  
 317 alum coagulation at their optimum doses (2 mL-MO/L and 4 mg-Al/L).

318 **3.4.2 Water quality**

319 Despite of the difference in coagulation-treated water quality between MO and alum coagulation,  
 320 water quality after MF treatment was comparable. For example, turbidity and colour in MF  
 321 permeate was not detectable or almost zero for both coagulants (**Table 2**), indicating that MF  
 322 treatment plays a major role in the reduction of turbidity and colour. In contrast, conductivity and  
 323 TOC in MF permeate varied notably due to the difference in coagulation performance (**Table 1**)  
 324 and the incapability of MF for their removal. MF membrane is not capable of removing  
 325 dissolved ions, resulting in the difference in conductivity in MF permeate (275 and 312  $\mu\text{S}/\text{cm}$   
 326 for MO and alum, respectively). Likewise, TOC in MF permeate of the MO treated river water  
 327 was as high as 15.3 mg/L, which was 2.9 mg/L higher than that of the alum-treated river water.  
 328 An advantage of MO over alum was water pH. Water pH is an important parameter in product  
 329 water to avoid damaging infrastructure in a water distribution network. MO coagulation followed  
 330 by MF treatment maintained water pH almost constant at 7.4, which is within the recommended  
 331 range of 6.5–7.5 by WHO guidelines.<sup>3</sup> By contrast, alum coagulation reduced the water pH from

332 7.4 to 6.3 (below the WHO guideline level), and it remained unchanged after MF treatment. This  
 333 necessitates pH adjustment by addition of chemical reagents, which is a cost factor.

334 **Table 2** – Water quality in MF permeate of raw river water, MO and alum treated-river water  
 335 with the optimum coagulant doses (2 mL-MO/L and 4 mg-Al/L) during the 1<sup>st</sup> filtration cycle:  
 336 The average and ranges of in in **Fig. 6** and **Fig. S3**.

Parameter	Untreated river water (control)	MO treated river water	Alum treated river water
Turbidity (NTU)	0.2 ± 0.1	0.0	0.0
Colour (PCU)	1.9 ± 0.1	0.3 ± 0.1	0.0 ± 0.0
Conductivity (µS/cm)	257 ± 1.0	275 ± 2.0	312 ± 2.0
TOC (mg/L)	15.3 ± 0.1	15.3 ± 0.1	12.4 ± 0.1
pH	7.4 ± 0.0	7.4 ± 0.0	6.3 ± 0.1

#### 337 **4. Conclusions**

338 Pre-treatment of the surface river with pre-filtered MO and alum at their optimum doses led to a  
 339 substantial reduction in membrane fouling. Despite of the relatively large difference in residual  
 340 turbidity after MO (1.1 NTU) and alum (0.1 NTU) coagulation, their membrane fouling levels on  
 341 MF treatment did not differ significantly over six filtration cycles. This indicates that sufficient  
 342 level of fouling mitigation in MF can be readily achieved through MO coagulation. Major water  
 343 quality (turbidity and colour) after MF treatment was comparable between MO and alum  
 344 coagulation. While MO coagulation slightly increased the load of organics, alum notably  
 345 increased conductivity. MO coagulation did not change water pH, which is advantageous over  
 346 alum coagulation, because post treatment for pH adjustment can be avoided. The results reported  
 347 here suggest that MO is a good alternative coagulant to mitigate membrane fouling of MF  
 348 treatment for decentralised drinking water applications.

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## 354 **6. Conflicts of interest**

355 There are no conflicts to declare.

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