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Preparation of nanoclay embedded polymeric membranes for the filtration of natural organic matter (NOM) in a circular crossflow filtration system

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1 **Abstract**

2 In-house and commercial membranes were used with different properties for humic acid separation
3 in a circular crossflow filtration system to determine the membranes' performances. The in-house
4 membranes were fabricated with the addition of bentonite nanoclay in Mendall,
5 polyvinylidene fluoride (PVDF), polyphenylsulfone (PPSU), polysulfone (PSF) and polyether sulfone
6 (PES) polymers. Bentonite nanoclay is recognized as a promising material for membrane applications
7 due to its ability to produce membranes with superior properties such as the mechanical strength,
8 large surface areas, adsorbing, antifouling and well-defined pore morphology. Three types of
9 commercial membranes were also used for humic acid removal from water. The morphology, surface
10 roughness, porosity and average pore size of the in-house and commercial membranes were then
11 compared. The XM50 commercial membranes showed smooth and even surface topography as
12 compared to other commercial and in-house membranes. The addition of bentonite into the polymer
13 changed the morphological structure, surface roughness, pore size of the polymeric membranes. Pure
14 water flux, permeate flux and rejection of humic acid were compared for in-house polymeric
15 membranes and commercial membranes in a circular crossflow filtration system. It was observed that
16 the fouling of humic acid was reduced by the addition of bentonite nanoclay in the in-house polymeric
17 membranes.

18

19 **Keywords:** *Membrane filtration; membrane fouling; nanoclay; water purification; circular crossflow*
20 *channel*

21

22 **1. Introduction**

23 Increasing industrialization has had an adverse impact on natural resources affecting the quality of
24 drinking water sources. The decreased availability of water has forced the humans to utilize
25 wastewater for drinking purpose after removal of pollutant and efficient water treatment [1, 2].
26 Natural organic matter (NOM) such as humic acid is available in surface water which causes several

27 issues such as colour, taste, odour and health problems. Membrane separation serves as a good
28 solution to solve these issues by providing an effective treatment and removal of humic acid. The
29 choice of the membrane materials in this regard is crucial as they can address the issue of fouling
30 caused by the pollutants from wastewater which otherwise may limit or stop the application of
31 membrane separation in such cases [3]. Hence, modifications to the membrane materials, either on
32 the surface or the internal morphology relating to the pore space, could help to enhance the membrane
33 performances and control membrane fouling [4]. A number of polymer and biopolymer materials
34 such as cellulose acetate (CA) [5], chitosan [6], polyvinylidenedifluoride (PVDF) [7],
35 polyphenylsulfone [8], polysulfone [9], polyethersulfone [10] have been developed already by
36 surface modification for removal of natural organic matter (NOM) like humic acid. PVDF is used as
37 a membrane material for ultrafiltration for humic acid separation because of its outstanding properties
38 of resistance towards chemical and membrane formation ability [7]. The antifouling property has
39 been studied using humic acid solution for modified polyphenylsulfone by polydopamine coating
40 ultrafiltration membrane [8]. Silica derived from rice husk and used as a modifier in the polysulfone
41 membrane for antifouling performance [9]. In this work, humic acid solution has been identified as a
42 major foulant for natural organic matter (NOM) for effective study of antifouling performance.
43 Polyethersulfone membranes were modified with hydrophilic monomers by phase inversion for
44 removal of humic acid [10]. A number of other investigations have also been done to modify the
45 PVDF, PPSU, PSf and PES membranes for effective removal and antifouling performance using
46 NOM. Literature reported that bentonite nanoclay was used as modifiers in membrane fabrication
47 [11-20]. Bentonite clay has smectite group with an arrangement of aluminium-phyllsilicate with
48 tetrahedral silica and octahedral alumina layers. Broadly, it is used in the wastewater treatment as an
49 adsorbent material. In an ore of clay, the main constitute of clay is found to be montmorillonite.
50 Membrane modifier like nanoclay (bentonite) has been proved to increase pore size, hydrophilic,
51 antifouling property in polymeric membranes, which has also increased the water permeate flux
52 through the membranes [12]. Naturally available nanoclay is therefore a potential modifier for the

polymer for water purification, which provides strong hydrophilicity, good chemical and mechanical strengths with low cost. Panpanit and Visvanathan [13] reported that the addition of bentonite in cellulose acetate has directed to enhanced hydrophilicity, porosity, permeability, antifouling property and effective control of the surface membrane properties. The addition of nanoclay increases the hydrophilic property of PVDF membrane and increase the water permeate flux through the membrane [14, 15]. The nanoclay can also increase the mechanical strength and thermal stability of the membranes [16-18]. According to the literature, nanoclay can control the porous morphologies within the membranes that can increase the clean water flux through the membranes [19,20]. The reason for the use of bentonite nanoclay for humic acids removal is constant ionic strength, bridging of bivalent metal ions between clay and humic acid. Furthermore, the dominant adsorption mechanism favours the removal of humic acid and enhancement of water flux. Hence, bentonite nanoclay was chosen for this study for polymer modification due to its low cost, antifouling property, hydrophilicity and removal of humic acid was not reported using bentonite nanoclay in all polymeric membranes.

In the present work, the fabricated in-house polymeric membranes with nanoclay were compared with the performance of commercial membranes to determine their performance in water and humic acid separation. Most of the current processes for the separation of humic acid are based on dead-end filtration which typically lead to concentration polarization and fouling. In dead-end mode, the flow of fluid is perpendicular to the filtration, so that water passes through the membranes while the solute particles are retained on the membrane surface, clogging and blocking the surface [21,22]. To overcome the blocking of dead-end filtration, a circular crossflow filtration system is used for NOM filtration in this work. The crossflow filtration system used to conduct all filtration experiments is discussed in previous studies in detail [23,24]. In the system, both Taylor and Dean vortices are formed, which help in reducing the concentration polarization and membrane fouling by producing secondary flows [23,24]. This paper aims to study the flux, rejection of humic acid and fouling effects of nanoclay embedded in-house polymeric membranes and commercial membranes in the same

crossflow filtration system [23,24]. The major issue faced by most crossflow systems is low contact time. Hence, the fluidic channels in the system where small fluid fluctuations are observed due to the increased surface effects are characteristics of the length-scale of the channel. The decreased velocity of fluid across the crossflow filtration system increases the contact time of the fluid with the membranes. Therefore, the main attempt in this work was based on the fabrication in-house membranes by addition of nanoclay in polymer blends, compare their performances with commercial membranes in circular crossflow filtration for permeate flux, humic acid solute rejection and fouling behaviour.

87

2. Experiment

89

2.1. Materials

The analytical grade polyvinylidene fluoride (PVDF), polyphenylsulfone (PPSU), polyamide-imides (PAI) and polysulfone (PSF), polyether sulfone (PES) (3000p) were purchased from Solvay Specialty Polymers Ltd, India. N-methyl-2-pyrrolidone (NMP), sodium dodecyl sulfate (SDS) (surfactant) was obtained from Merck Specialties Ltd., India. K⁺- Bentonite nanoclay was purchased from Sigma-Aldrich India limited. A sample SEM image of the bentonite nanoparticles is shown in Fig. 1. Commercial membranes (PM10, XM300, XM50) were purchased from Amicon™ (Massachusetts, USA). Humic acid particles were procured from M/s. Loba Cheme, India. Double distilled (DD) water was prepared in the laboratory for use in all experiments.

99

2.2. Fabrication of nanoclay based in-house polymeric membranes

Nanoclay embedded polymeric membranes were prepared by phase inversion process. The fabrication procedure is described below, which is also shown schematically in Fig. 2.

103

104 The dope polymer solution was prepared with 16.5% polymers, 1% nanoclay, and 82.5% solvent on
105 a weight basis. N-methyl-2-pyrrolidone (NMP) was used as the solvent and bentonite was used as the
106 nanoclay for the membrane modification. The nanoclay size ranges between 50-250 nm with an
107 average particle diameter of 179 nm (SD: ± 79 nm). The in-house polymeric membranes were
108 fabricated with polyether sulfone (PES), polyvinylidene fluoride (PVDF), polyphenylsulfone
109 (PPSU), polyamide imide (PAI), poly-sulfone (PSF). Sodium dodecyl sulfate was used as the
110 surfactant during the membrane formation and was diluted with deionized water (DI) water at
111 concentrations of 2%. The 1 wt% bentonite and 82.5% NMP mixture was sonicated in an ultrasonic
112 bath for 3 h to ensure uniform dispersion of the bentonite particulates in the solvent. 16.5% of all
113 polymers was added individually into the complete dispersed bentonite and NMP mixture and
114 accompanied by constant magnetic stirring at 400 rpm for over 24 h using ultrasonicator (model: Bath
115 sonicator, PCI Analytics). The homogeneous solution was then allowed to eliminate air bubbles in an
116 hour. The solution is then cast into thin films of 250 μm thickness over a clean, leveled glass plate
117 using a stainless-steel film applicator at 50% humidity and 25°C temperature. The film was kept for
118 30s to evaporate the solvent, then exposed to a surfactant bath at 15°C for 1 h. The membranes are
119 kept in water for 24 h before subsequent storage in formalin. The outline of the membrane fabrication
120 process is shown in Fig. 2.

121

122 **2.3. Commercial membranes**

123 Commercial membranes were used to compare the performance of the *in-house* membranes
124 developed in this work. XM300 and XM50 are modified polyacrylic fibrous membranes, while PM10
125 is a hydrophilic polysulfonic membrane.

126

127 **2.4. Membranes characterization**

128 In order to analyse the surface morphology of the membranes, SEM micrographs of the membrane
129 surfaces and cross-sections were obtained by using a field emission gun scanning electron microscope

130 FEG-SEM (Leo (Zeiss) 1530-VP) equipped with X-ray energy dispersive spectroscopy (X-EDS)
 131 system. The membranes were coated with a gold-palladium sputter coating prior to the analysis. The
 132 SEM accelerating the voltage was set at 20 kV and the images were procured at 1kX, 10kX and 25kX
 133 magnifications. The pore radii and fiber characteristics of the membranes were calculated by
 134 processing the SEM micrographs (Table 1). The elemental compositions of the surface of the
 135 membranes were analyzed using X-ray energy dispersive spectroscopy (EDS) before and after the
 136 filtration process. The composition of the debris after the filtration experiments gives an insight into
 137 the performance of the membrane. The SEM micrographs were therefore analysed further with the
 138 help of an image processing software, namely ImageJ 1.38e, Adobe Photoshop CC 2015, and
 139 MATLAB R2016a, to calculate the membrane porosity values [25]. The porosities calculated from
 140 the image processing step are supplemented with experimental results. A 1 cm² cut was made on the
 141 membranes, which was then kept in an ultrasonic bath in distilled water for 30 min. The weights of
 142 the membranes were immediately measured after they were taken out of the water bath, and the wet
 143 weights of the membranes are obtained. The membranes are then dried for a day under ambient
 144 conditions. The membrane weights measured provided the dry weight of the membranes. The porosity
 145 of the membranes (ε) is calculated according to equation [26],

$$146 \quad \varepsilon = \frac{(w_1 - w_2) / \rho_{water}}{w_2 / \rho_{membrane} + (w_1 - w_2) / \rho_{water}} \quad (1)$$

147 where w_1 is the total weight of the membrane and liquid in the membrane, w_2 is the weight of the
 148 dried membrane, ρ_{water} is the density of water, $\rho_{membrane}$ is the density of the membrane.

149

150 The overall surface roughness and 3D morphology were studied by using Veeco Explorer AFM (now
 151 owned by Bruker Corp) at tapping mode (TM-AFM) using a silicon probe at a high resonance
 152 frequency. The surface roughness was expressed by a root-mean-square roughness while the average
 153 roughness was calculated by the following equations:

$$154 \quad R_a = \frac{1}{n} \sum_{i=1}^n |y_i| \quad (2)$$

$$R_{rms} = \sqrt{\frac{1}{n} \sum_{i=1}^n y_i^2} \quad (3)$$

where R_a is average roughness, R_{rms} is the root mean square roughness, n is the number of points in the sample area, y_i is the surface height. The scanning area of each membrane was $10 \mu\text{m} \times 10 \mu\text{m}$. It is assumed that the chosen sample surface ($10 \mu\text{m} \times 10 \mu\text{m}$) represents the surface of the membrane. The calculated data indicate the roughness on the membrane surfaces, as discussed in Section 3.

2.5. Membrane filtration performance

2.5.1. Circular crossflow filtration cell

Filtration experiments are conducted (Fig. 3(a)) to measure the flow and rejection characteristics of humic acid through the chosen membranes. The circular crossflow filtration cell (600 mL volume) purchased from AMICON, Massachusetts, USA has an effective membrane surface area of 40 cm^2 . The flow in the cell is achieved by a peristaltic pump which is acquired from Watson-Marlow Ltd, Cornwall, UK. The system is pressurized by compressed air and controlled using manual control valves. A humic acid solution is maintained as a homogenous suspension by utilizing a stirrer. The pressurized feed (Fig. 3(b)) enters the filtration cell and flows through a circular crossflow channel consisting of 3 spirals. The channels have a maximum radius of 4.1 cm and a minimum radius of 1 cm. The spiral fluidic channel was characterized, and the structure of the channel was determined using surface metrology. A coordinate measuring instrument, Talysurf CLI 2000 (LK ultra-Carnio studio), was used to determine the geometry of the system (Fig. 4). The width, height, and length of the channel and the conical height of the device are measured. These are found to be $9.5 \pm 0.3 \text{ mm}$, $0.363 \pm 0.005 \text{ mm}$ and 760 mm, respectively. The feed entering the spiral channel flows through the membrane under the channel, which rejects a fraction of the feed while allowing a part to permeate through it. The retentate is recycled back to the feed reservoir. The pressure gauges are utilized to measure the pressure at feed inlet, retentate outlet, permeate outlet, and channel inside.

181 **2.5.2. Permeate flux of humic acid**

182 Steady states are attained for the membranes at around 20 min. The flux of the system is calculated
183 according to the equation [23]:

$$184 \qquad \qquad \qquad \textit{Permeate Flux} = \frac{\textit{Permeate Volume}}{\textit{Time} \times \textit{Effective Membrane Area}} \qquad (4)$$

185 The rejection % of the membranes for the system was analyzed by calculating the concentration of
186 humic acid in the permeate. The permeate concentrations are determined using a spectrophotometer
187 (model: mini 1240 UV-VIS, Shimadzu, Milton Keynes, UK), which measures the absorbance at a
188 wavelength of 254 nm. The permeate concentrations are calculated with the prepared humic acid
189 solutions as the standard. The turbidity of the solutions was obtained using a μ TPW turbidity meter.

190

191 **2.5.3. Fouling studies**

192 The clean membranes are pretreated by soaking in deionized water for one hour, with water being
193 replenished every 20 min. The feed is sonicated using an ultrasonic water bath for about 60 min at
194 22°C ($\pm 2^\circ\text{C}$) to homogenize the humic acid solution. The membranes are carefully placed under the
195 circular crossflow channel with the glossy side facing up. The peristaltic pump is utilized to initiate
196 a constant velocity flow in the filtration cell. The pressure of the feed inlet is controlled manually by
197 using a pressure value. The filtration was run for 80 min, and samples of permeate are collected at
198 regular intervals of 2 min. The pressure of the system is altered every 20 min where it is initially kept
199 at 1 bar, then raised to 1.5 bars before decreasing it back to 1 bar and then subsequently increasing
200 again. Filtration experiments are performed for all the membranes. A 40 mg/L solution of humic acid
201 is prepared to run in the filtration system. The humic acid concentration in the feed was chosen based
202 on typical free carbon content of in rivers [27].

203

204 3. Results and Discussion

205 3.1. Morphologies of in-house and commercial membranes

206 The surface and cross-sectional morphologies of the in-house and commercial membranes are shown
207 in Fig. 5, 6 and 7. It is evident that 1 wt.% bentonite in polymers changed the morphologies of the in-
208 house membranes. All polymeric membranes showed macroporous and microporous pores on the
209 surface of the membrane. The overall membrane surface morphologies were also significantly
210 affected by the addition bentonite. In particular, the pore formation and pore size were found to be
211 enhanced for PSf and PES polymeric membranes. As depicted in Fig. 5, the top surface of Mendall
212 polymer has a denser pore structure, which is due to the delayed de-mixing during the phase inversion
213 process. In Fig. 5, the surface of membranes through the SEM images indicate that the all membranes
214 are well tailored by bentonite nanoclay.

215

216 It is evident that nanoclay membrane morphology is characterized by a superficial layer with macro-
217 pore, a bottom layer which has a sponge-like pore structure with micro-pores and an intermediate
218 layer, with finger-like pores and micro-pores [28]. Membranes are found to have an elongated finger-
219 like macroporous structure followed by a sponge-like microporous structure (Fig. 6). This provides
220 improvement to the high rejection, which is observed in the membranes due to the compacted nature
221 of the small microporous layer. However, Mendall™ polysulfone is found to have a wafer-like
222 spongy microporous structure. This leads to a high flow rate since the micropores present in the
223 membrane are large. It is also observed that all the porous membranes except Mendall™ polysulfone
224 have a pore size that are in the ultrafiltration range. Hence, these membranes show a large rejection
225 percentage for the humic acid particles, which is composed of particles in the size range of 0.1 – 100
226 μm . The crossflow nature of the flow causes the water to seep through the layers of membranes and
227 seem to thicken them, most likely, due to their hydrophilic nature. A change in the pore structures is
228 also observed (Fig. 6) due to the presence of large macropores in the membranes. A reduction in the

size of the pores is observed due to the encapsulation of pores resulting from fluid flow. This further explains the reason as to why the rejection is found to increase with pressure.

As observed in Table 1, the average pore size of the membranes increases due to the addition of nanoclay. This is likely to affect the fouling and, hence, the filtration efficiencies of the membranes, as well as other factors such as their wetting characteristics. We discuss how the addition of nanoclay affects the fouling and filtration efficiencies of the membrane in the latter part of the paper. However, this work did not carry out any measurements on the wetting characteristic of the membrane during the filtration experiments. This is because we are of the opinion that the typical ex-situ measurements techniques for wetting characteristic (e.g., contact angles) may not represent the in-situ conditions within the filtration set up closely enough.

3.2. EDS mapping of in-house membranes

The presence of bentonite nanoclay in the membrane structure was confirmed by energy-dispersive X-ray spectroscopy (EDS) mapping (Fig. 8). Silicon (due to the presence of nanoclay particles), aluminum, sodium, magnesium, potassium, titanium and iron were observed in the polymeric membrane structure. Bentonite is a clay mineral which consists of aluminum silicates, iron, magnesium, sodium, potassium, and iron. Hence, most of the elements on the membrane surface were carbonaceous or metal ions. These are accumulated due to irregularities on the polymer surface, storage of membranes in water, and facilitate the adsorption of humic acid and transport water through the membranes. It is also verified that the elemental composition of the initial concentration of polymer solution and that of the final membrane manufactured are similar, showing homogeneity exhibited by the membrane manufacturing process.

3.3 Porosity values of in-house and commercial membranes

254 The porosity values of the membranes calculated through membrane weighing and image processing
255 method are illustrated in Fig. 9. The measured porosity of XM 30 membrane has the highest value
256 when compared with other membranes. For all in-house membranes, PSf membrane has the highest
257 value when compared. The higher porosity of the membranes is attributed to the delayed
258 solidification, solubility parameters of the non-solvent–polymer system. Hence, the porosity of the
259 membranes can be controlled by bentonite nanoclay in polymeric membranes e.g. the coagulation.
260 However, the porosity measurement by image processing and wet method are varying the values of
261 all the membranes. The nanoclay particles are dispersed in the DMF solvent. When the polymer
262 solution and clay suspensions are mixed, the polymer chains intercalate and displace the solvent
263 within the interlayer of the clay, which then evaporates [29]. As seen in SEM images, the addition of
264 nanoclay results in membranes with thinner skin layer and higher porosity when compared with
265 polymeric membranes. Water flux of nanoclay embedded membranes also increases significantly
266 [30]. In some of the cases, where the membrane surfaces have prominent 3D surface topologies (e.g.,
267 PAI and PSF), the image processing tool may not provide a very accurate interpretation of the porosity
268 values. This is evident in Fig. 9.

270 **3.4 Surface roughness of in-house and commercial membranes**

271 AFM is useful and versatile tool for membrane surface characterisation. The surface roughness of in-
272 house membranes was analysed from AFM images and are shown in the supporting information S-
273 Fig. 1. The images show the distribution of the nanoclay particles on the surface of the membranes,
274 indicated by the white spots which represent the nanoclay particles. The nodular surface morphology
275 in the images also suggest that the nanoclay particles are dispersed fairly uniformly in the polymer
276 blend promoting a uniform enhancement of roughness throughout the membrane surface. The surface
277 roughness is considered as a measure of fouling of the membrane surface. Mendall™ polysulfone is
278 found to have the largest roughness factor, which amounts to a high degree of fouling on its surface,
279 as seen above. Statistical analyses show the average roughness of the commercial membranes from

the AFM images which are included in the supporting information (S-Fig. 2). The commercial membranes are found to have marginally smoother surface as compared to the in-house membranes. The 3D views of AFM images of the in-house and commercial membranes are shown in Fig. 10 and 11. All the images showed the changes of membrane physical structure of the surface and roughness. The addition of nanoclay in the polymers network changes in surface roughness with alteration of physical surface profile. In particular, when the PSf membranes were modified with nanoclay, the pore-diameters were observed to become larger. The root-mean-square of the roughness and average roughness factors were calculated and shown in Fig. 12. As evident the roughness increases due to the surface area of clay particles. In particular, the PSf membranes showed higher root-mean-square roughness and average roughness values. The reason for the increase in the roughness is mainly due to the hydrophobicity of the PSf membranes [31]. Furthermore, the bentonite being more loosely packed during the casting conditions, it leads to greater surface roughness. Hence, the fouling are reduced during the use of in-house membranes as compared with the existing commercially available membranes. These roughness results confirmed the efficacy of the in-house membranes in cleaning, removing foulant and adsorbent from membrane surfaces. The rougher surfaces fouled more most likely due to the effects of increased colloidal interactions and adsorption on the membrane surface.

296

297 **3.5 Humic acid separation performances of in-house and commercial membranes**

Humic acid flux and rejection experiments were conducted for PVDF, PES, Mendall membranes and commercial membranes on the circular crossflow systems. The dry humic acid particles and particle size range is shown in Fig. 13. Among the commercial membranes, XM 300 showed higher permeate flux for humic acid solution (Fig. 14 (b)). In the case of in-house membranes, Mendall-bentonite membrane showed higher permeate flux for humic acid solution (Fig. 14 (a)). As shown in Fig. 15 later, the higher humic acid rejection was found for PVDF-bentonite and PM 10 membranes. There are the two key factors for higher rejection, one is size exclusion of humic acid with respect to the shapes and hydrodynamic sizes. Next, the increase of repulsion between humic acid and bentonite

306 incorporated PVDF membranes. Porous membranes (Mendall™ polysulfone) that have large flux are
307 found to have the least rejection, whereas polyvinylidene fluoride is found to have the highest
308 rejection suffers from the lowest flux. Permeate flux is found to be more in the case of clean water
309 than the humic acid due to the accumulation of humic acid particles on the surface of the membranes.
310 These particles cause a net decrease in the porous nature of the membranes, which in turn curbs the
311 flow of flux through the system. It is ascertained from the experiments that as the size of pores
312 increase, the flux through the membranes increases, and the rejection decreases. This is due to the
313 increase in pore size of membranes allowing more flux as well as larger particles to pass through the
314 membrane. According to the literature, humic acid have monodisperse particle and they may contain
315 a central "core" with a different structure [32]. The interaction of bentonite and humic acid from the
316 aqueous solutions for humic acid removal was reported for polyacrylamide/bentonite composites
317 [33].

318

319 **3.6 Fouling behavior of in-house and commercial membranes**

320 The fouling studies of the in-house and commercial membrane were conducted using humic acid
321 solution and demineralised water. The fouling experiments were carried out with reference to the
322 fluxes of humic acid and water through the membrane. As shown in Fig. 14 (a and b), the permeate
323 flux of step two is found to differ from that of step one. This change in flux is due to a change in the
324 pore characteristics that are attributed to multiple factors such as the accumulation of particles on the
325 membrane surface and the effects of the momentum of fluid flow through the pores. Most membranes
326 have a constant flux during the filtration process during step I and step II. Membranes are found to
327 attain a steady-state flux within the 20 min of the experiment. Hence, the circular crossflow filtration
328 system could effectively reduce particle accumulation on the surface of the membrane, which protects
329 the membranes against fouling (which would cause a decrease in flux). However, Mendall™
330 polysulfone has a significant decrease in flux. This is attributed to the high flux characteristics due to
331 which the momentum of the water particles can cause a more significant decrease in flow over time.

332 As mentioned above, the observations could be explained by the change in the pore size of the
333 membranes. High pressure increases the momentum of fluid on the surface of the membranes, in turn,
334 increasing the pore size of the membrane. It is also observed that time has an inertial effect on the
335 membrane pore structures. When the pressure is reverted to 1 bar (run 1) after operating in 1.5 bar
336 (run 2), the flux increases. This is because the pore sizes remain in their original sizes (as when the
337 system is started). Ahmad et al [34] investigated the effect of membrane morphology, pore size, and
338 porosity on fouling behavior of humic acid solution through PES membrane with different loadings
339 of TiO₂ as the nano material. It is concluded that the strength of pores and their resistance to shear
340 forces is pivotal to the efficiency of the membranes. The more resilient the pore is to changes in its
341 surroundings, the longer the life of the membrane. Fouling of membrane is another factor to be
342 minimized, that directly reduces the flow of the membrane. The humic acid flux of PES-bentonite
343 membrane was significant dependence on pore size of the membrane. However, the humic acid
344 deposits and tighter packing of the humic acids within the deposit on surface of the membrane may
345 cause the decline of flux during cross flow filtration.

346

347 **3.7. Turbidity of the permeate from using in-house and commercial membranes**

348 The turbidity of humic acid in permeate through in-house and commercial membranes was compared
349 with 1 and 1.5 bar pressure in cross flow filtration. This is illustrated in Fig. 16 which shows the
350 change in turbidity of membranes as a function of pressure. It is seen that PM10 and PVDF
351 membranes had lower turbidity in permeate in both 1 and 1.5 bar pressure. The rejection percentage
352 was further correlated with the turbidity of the solution. The turbidity of the permeate means that
353 humic acid substances passes through the membrane in the permeate. The bentonite incorporated
354 Mendall membrane is having average pore size of 8.375 μm which is higher than other membranes
355 (Table 1). The permeate flux for humic acid is also higher than other membranes. When humic acid
356 solution was passed through the crossflow filtration system, humic acid molecules were adsorbed on
357 the membrane surface due to the presence of bentonite. As an example, the adsorbed humic acid on

358 the Mendall membrane surface is shown in Fig. 17. At 1 and 1.5 bar pressure, the humic acid particles
359 transfer very fast through the internal pores of Mendall membrane. Hence, the Mendall membrane
360 showed higher value of turbidity in the permeate. This is because the humic acid partially dissolves
361 in water, it still contains a lot of suspensions which remain in the permeate. These suspensions cause
362 the muddy brown color in the solution, which increases the turbidity.

363

364 **4. Conclusion**

365 It is found that the performance of the in-house nano-porous membranes is comparable to the
366 performance of commercially available membranes. The in-house membranes show low fouling, high
367 flux rate and low retention favoring their potential applications in water purification. Of the in-house
368 membranes, a high average pore size of 8.375 μm was observed for Mendall-bentonite membrane
369 which is higher than all other in-house and commercial membranes. In addition, the surface and cross-
370 sectional morphology of membranes with different orientation in presence of nanoclay showed the
371 impacts on humic acid separation in cross flow filtration. Bentonite in polymeric membranes was
372 highly effective in changing the membrane surface roughness favouring the interactions of the
373 membrane surface with humic acid particles. The chosen commercial membranes, namely, PM10,
374 XM50 and XM300, had smother surface topography than the in-house membranes. From the fouling
375 studies, it can be concluded that the introduction of the charged bentonite nanoclay for polymeric
376 membranes modification with different surface roughness are the main targets to reduce undesirable
377 fouling. Therefore, these membranes have prospects of being specialized for their specific application
378 with the addition of nanoclay. Further analysis of a broader range of nanocomposite-based
379 membranes is to be analyzed in the future.

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Fig. 1. SEM image of nanoclay particles.

Fig. 2. Schematic representation of fabrication process of in-house membranes.

Fig. 3. (a) The experimental set up of the circular crossflow filtration system, (b) the side view of the filtration cell.

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Fig. 4. Depth profile of the plate consisting of fluidic channels used in the filtration experiments.

Fig. 5. Top surface morphology of in-house membranes

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Fig. 6. Cross sectional morphology of in-house membranes

Fig. 7. Surface and cross-sectional morphology of commercial membranes

Fig. 8. EDS mapping of components for PVDF membrane at 10kX magnification, the element of concern is shown on the top of each image.

Fig. 9. Porosity of the membranes calculated through experiments and image processing (SD from duplicate samples from one of three representative experiments).

Fig. 10. AFM surface images of in-house membranes

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Fig. 11. AFM surface images of commercial membranes

Fig. 12. Surface roughness of in-house and commercial membranes

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Fig. 13. (a) SEM micrographs of dry humic acid particles, (b) humic acid particle size range.

Fig. 14. Permeate flux and fouling of (a) in-house membranes (porous membrane), (b) commercial membranes (fibrous membrane).

Fig. 15. Percentage rejection of humic acid for various membranes with respect to time (SD from duplicate samples from one of two representative experiments).

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640 **Fig. 16.** Turbidity of the permeate for various membranes at two different pressures (SD from
641 duplicate samples from one of three representative experiments).

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646 **Fig. 17.** Humic acid particles on the surface of membrane Mendall™ polysulfone after filtration.

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648 **Table. 1:** Average Pore Size, fiber-fiber distance, fiber diameter of in-house and commercial
649 membranes
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Membrane Type	Average Pore Size (μm)	Average Fiber-Fiber Distance (μm)	Average Fiber Diameter (μm)
PM10	0.004 ± 0.134	3.093 ± 1.909	3.293 ± 2.209
XM50	0.0053 ± 0.210	9.958 ± 5.723	5.484 ± 5.074
XM300	0.0086 ± 0.132	15.640 ± 12.724	9.352 ± 8.675
Poly-ether-sulfone	0.553 ± 0.272	--	--
Mendall™	8.378 ± 4.196	--	--
polysulfone			
Polyvinylidene fluoride	0.481 ± 0.230	--	--
Poly amide imide	0.463 ± 0.242	--	--
Polysulfone	0.663 ± 0.349	--	--
Polyphenylsulfone	0.344 ± 0.218	--	--

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**Preparation of nanoclay embedded polymeric membranes for the filtration of
natural organic matter (NOM) in a circular crossflow filtration system**

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Supporting Information

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S. Fig1. AFM images of in-house membranes to show the average roughness

S. Fig.2. AFM images of commercial membranes to show the average roughness