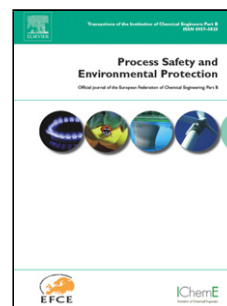


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1 **Understanding the risk of scaling and fouling in hollow fiber**
2 **forward osmosis membrane application**

3 **Highlights:**

- 4 • Driving force in FO does not remain constant unlike in pressured membrane
5 processes.
- 6 • UF/RO fouling assessment method may not be suitable for FO.
- 7 • An alternate fouling evaluation process is suggested for FO membrane application.
- 8 • In active layer–draw solution, rapid flux decline is not linked to FO fouling.
- 9 • The crossflow rate plays an important role for varying fouling effects for FO.
- 10
- 11
- 12
- 13

1 Understanding the risk of scaling and fouling in hollow fiber

2 forward osmosis membrane application

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12 13 Abstract

14 Fouling studies of forward osmosis (FO) were mostly conducted based on fouling evaluation
15 principals applied to pressure membrane processes such as reverse osmosis (RO)/
16 nanofiltration (NF)/ microfiltration (MF)/ ultrafiltration (UF). For RO/NF/MF/UF processes,
17 the single flux driving force (hydraulic pressure) remains constant, thus the fouling effect is
18 easily evaluated by comparing flux data with the baseline. Whilst, the scenario of fouling
19 effects for FO process is entirely different from RO/NF/MF/UF processes. Continuously
20 changing driving force (osmotic pressure difference), the changes in concentration
21 polarization associated with the varying draw solution/feed solution concentration and the
22 fouling layer effects collectively influence the FO flux. Thus, usual comparison of the FO
23 flux outcome with the baseline results can not exactly indicate the real affect of membrane
24 fouling, rather presents a misleading cumulative effect. This study compares the existing FO

1 fouling technique with an alternate fouling evaluation approach using two FO set-ups.
2 Scaling and fouling risk for hollow fiber FO was separately investigated using synthetic
3 water samples and model organic foulants as alginate, humic acid and bovine serum albumin.
4 Results indicated that FO flux declines up to 5% and 49% in active layer-feed solution and
5 active layer-draw solution orientations respectively.

6

7 **Keywords:** Concentration polarization; Flux; Hollow fiber forward osmosis membrane;
8 Inorganic scaling; Organic fouling

9

1

2 **1. Introduction**

3 Forward osmosis (FO) is a new low cost desalination approach utilizing natural osmotic
4 pressure gradient between draw solution (DS) and feeding solution (FS) (Cath et al., 2006,
5 McCutcheon et al., 2005, Sahebi et al., 2015). Due to its low pressure operation and low
6 energy process requirement, FO has been gaining wide popularity and effectively used for
7 water desalination, juice concentration, oil and gas wastewater treatment and energy
8 production (Elimelech, 2007, Kessler and Moody, 1976, Bamaga et al., 2009, Chung et al.,
9 2012, Warczok et al., 2007). At present, the FO process is being evaluated for commercial
10 applications after gone through early lab-scale test.

11

12 Membrane fouling is the accumulations of the inorganic, organic or microbiological
13 impurities on the membrane surface, which significantly affect the membrane performances
14 in terms of flux and salt rejection. It not only influences the quality of the product water but
15 also directly affects the operating cost such as downtime, cleaning chemical costs, labour
16 requirements, production loss and frequent membrane replacements (Peng et al., 2004). The
17 fouling is a very complex phenomena as it is determined by various physical and chemical
18 interactions between different foulants and membrane materials (Kim et al., 2010, Saffarini et
19 al., 2012). Since fouling is considered as a serious operational issue for all membrane based
20 systems, the FO fouling studies are also important to evaluate the risks associated with
21 commercial operations of the FO system. Various studies have been published with the
22 evaluation of the fouling potential for various types of FO membranes under different feed
23 and draw solution combinations (Cornelissen et al., 2008, Mi and Elimelech, 2008, Achilli et
24 al., 2009, Mi and Elimelech, 2010, Gu et al., 2013). Fouling may occur on the membrane
25 surface, at the pore openings and within the pores (Arkhangelsky et al., 2012). Some of the

1 key factors controlling fouling mechanism are foulant characteristics, DS and FS chemistry
2 (pH, ionic strength, and divalent cation concentration), membrane properties (surface charge,
3 hydrophobicity, and roughness), and hydrodynamic conditions (permeate flux, and crossflow
4 velocity) (Bellona et al., 2004, Peng et al., 2004, Greenlee et al., 2009, Radu et al., 2012,
5 Pérez-González et al., 2012).

6
7 Earlier studies on FO fouling found that the severity of the fouling potential for FO
8 membranes was not so intensive. FO, being a process governed by the osmotic pressure
9 gradient, has been hypothesized to have a lower fouling propensity than other pressure driven
10 membrane processes, such as reverse osmosis (RO)/nanofiltration (NF) (Li et al., 2012,
11 Zhang et al., 2012). Mi et al. (2010) evaluated the FO fouling potential with alginate and
12 found that FO fouling is fully reversible with simple rinsing (without any cleaning reagents).
13 In addition, fouling reversibility in FO was attributed to the less compact organic fouling
14 layer formed on the membrane surface due to the lack of hydraulic pressure (Zhao et al.,
15 2012, Park et al., 2013).

16 Gu et al. (2013) assessed FO fouling potential with opposite charged foulant mixtures and
17 suggested that membrane surface properties played a less important role in fouling due to the
18 dominance of foulant-foulant interaction. Further, under mild fouling conditions, the thin film
19 composite (TFC) membrane was more prone to fouling due to the much rougher membrane
20 surface. Tang et al. (2010) indicated that the flux loss in active layer-feed solution (AL-FS)
21 orientation was likely due to the combined effects of (1) the internal clogging of the FO
22 support structure as well as (2) the enhanced internal concentration polarization (ICP) caused
23 mainly by the reduced porosity and mass transfer coefficient in the support layer (SL). Peng
24 et al. (2004) found that biofouling layer is more stable and difficult to remove by flushing as
25 crossflow rate was increased from 4 cm/s to 33 cm/s for 1 h of operation.

1

2 Most of these studies identified that FO showed consistent performances at AL-FS
3 orientation and avoid severe fouling (She et al., 2012, Valladares Linares et al., 2014). FO
4 test by Yip et al. (2011) in active layer–draw solution (AL-DS) orientation when used to
5 harvest salinity gradient power noticed that osmotic backwash facilitated the FO flux
6 restoration.

7

8 It is however observed in these studies that the FO fouling was evaluated following the
9 fouling principles of RO, NF, ultrafiltration (UF), or microfiltration (MF), where the
10 performance of these systems is compared with the baseline outcome and the deviation in
11 their flux performance is referred as to fouling effects. The RO/NF/MF/UF is operated for a
12 fixed driving force (hydraulic pressure). However, the FO process differs from the other
13 membrane-based processes, mainly in terms of the non-existence of a constant driving force
14 during the experiment run. Unlike RO or NF, FO may not be operated at a fixed driving
15 force. Further, permeate flux and trans-membrane pressure is the best indicator of
16 RO/NF/MF/UF membrane fouling applications but not used for FO process at all.
17 Comparisons of the resultant flux trend with the baseline outcome easily figured out any
18 performance variations for RO/NF/MF/UF, which clearly indicated the resultant fouling
19 effect on the membrane performance.

20

21 However, at any fixed time, as the FO does not show the same driving force for any two flux
22 data curves, the standard flux curves comparison is hardly able to identify the portion of flux
23 change that is influenced by fouling (**Fig. 1**). For FO, at any particular point, the continuously
24 changing driving force (due to the varying FS and DS concentrations) with their simultaneous
25 effects on the concentration polarization (CP) make it really hard to operate two FO processes

1 having similar driving force. For particular FO applications, the FO membrane is also used in
 2 AL-FS and AL-DS orientations with varying nature of performances. Additionally, as FO
 3 manages the simultaneous flow of two different solutions as FS and DS on either side of the
 4 membrane it carries varying fouling risks for different sides of the membrane. FS coming

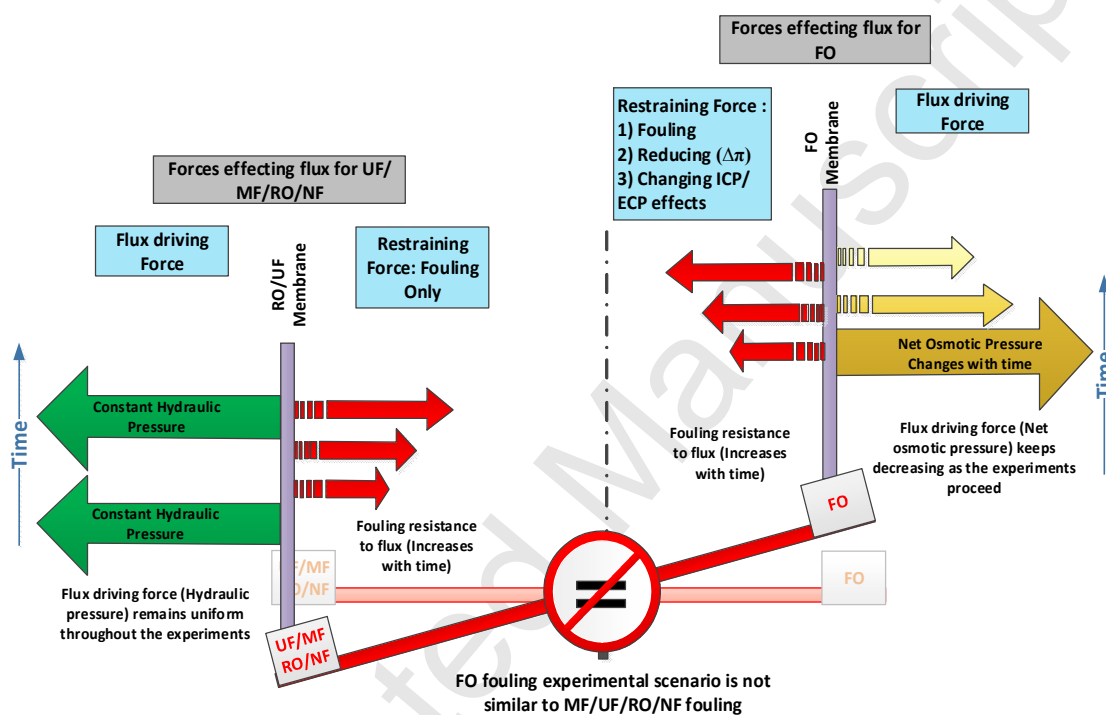


Fig. 1 Comparison of the fouling scenario between FO and RO/NF/MF/UF processes. FO operates under the influence of constantly varying driving forces whereas for RO/NF/MF/UF processes, the main flux driving force (hydraulic pressure) remains constant for the whole test run. Hence the existing fouling experimental protocol may not be used to evaluate fouling effects for FO membrane as it gives misleading outcome.

5 from various sources carry different impurities which pose severe threats for fouling
 6 development on the FO membrane surface, whereas the risk of fouling on the DS side is
 7 found to be minimal

1 because the DS is usually prepared in a controlled working environment by dissolving
2 suitable draw solute in high quality treated water. Thus, FO fouling in AL-DS orientation has
3 not been fully evaluated in previous FO studies (Holloway et al., 2007, Mi and Elimelech,
4 2008, Cornelissen et al., 2008, Zhang et al., 2012).

5
6
7 The comparison of the fouling evaluation approach for FO and RO/NF/MF/UF indicated that
8 these basic differences between the FO and other membrane system and their approach
9 towards their fouling processes were not realized in earlier studies. Thus, the existing
10 comparison of the flux performances for FO fouling which rely on the comparison of the flux
11 performance curves with the baseline failed to indicate actual fouling potential for any FO
12 operation. To overcome this issue, this study suggests a modified approach, referred as (Tahir
13 approach). Tahir approach takes all forces affecting the flux in the hollow fiber FO
14 membrane fouling process into account and clearly indicates actual flux loss by fouling.

15
16 This study evaluated and compared the risks of scaling and fouling in the hollow fiber FO
17 (HFFO) membrane application using two different fouling approaches: 1) the existing
18 commonly used approach and 2) Tahir approach. The fouling of FO membrane was also
19 evaluated using various synthetic FSs mixed with model organic foulants such as sodium
20 alginate, humic acid (HA) and bovine serum albumin (BSA).

22 **2. Materials and Methods**

23 **2.1 FO setup**

24 **Fig. 2** shows the sequence of experiments performed to investigate the effect of fouling for
25 FO membrane. Two identical bench scale HFFO set-ups, similar to the one reported by

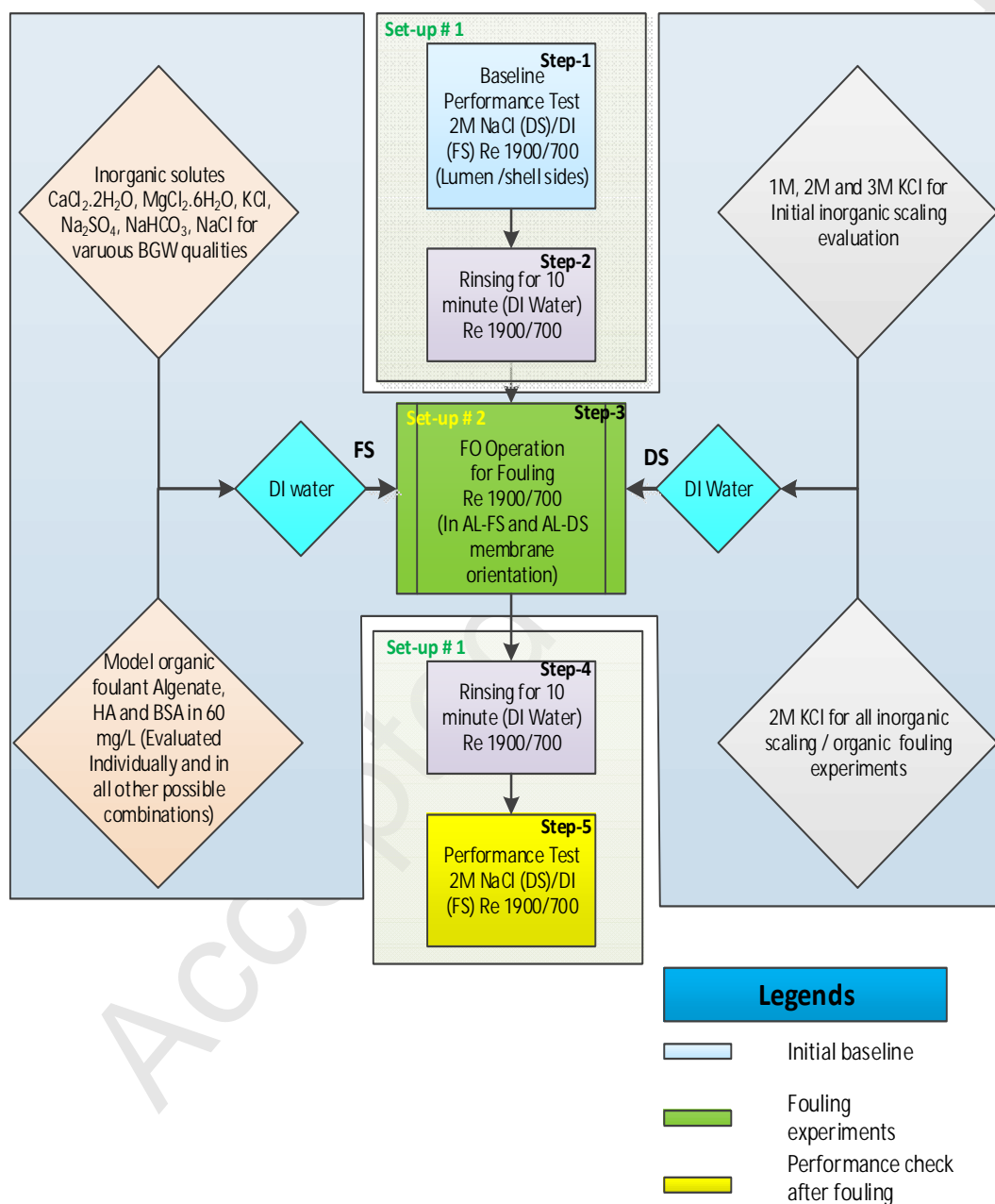
1 Majeed et al. (2013) were used. Each set-up used two Cole-Parmer variable speed pumps to
2 circulate DS and FS through the membrane module. A temperature controller unit linked to a
3 water bath was used to maintain the temperature of the DS and FS sides at $25\pm 0.5^\circ\text{C}$. All
4 fouling tests were performed at FO set-up # 2 for similar crossflow rates representing a
5 Reynolds number (Re) of 1900 and 700 for the lumen side and shell side, respectively. Set-up
6 # 1 was used to evaluate the performances of the new membrane and effect of fouling on
7 HFFO membrane.

8 **2.2 Membrane**

9 HFFO lumens manufactured by Samsung Cheil Industries, Korea were used to construct
10 different modules for the study, each carrying a membrane area of 25 cm^2 . FO lumens were
11 made up of aromatic polyamide (PA) thin film composite (TFC) active layer (inside) on
12 hydrophilic sulphonated polysulphone (SPSf) substrate (Chen et al., 2014, Majeed et al.,
13 2013). The PA membrane carried a negative charge of -9.30 mV at $\text{pH}=7$ with contact angle
14 of 55° (Majeed et al., 2013). FO membrane properties such as pure water permeability (A) and
15 salt rejection (B) have been reported in another earlier study (Majeed et al., 2013). The
16 fouling performances of the HFFO membrane modules were evaluated in both AL–DS and
17 AL–FS membrane orientations. For AL–FS orientation, the FS passed through the inner side
18 of lumens and the DS run outside the lumens, while the FS and DS run the opposite way for
19 AL–DS membrane orientation.

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Fig. 2 Sequence of operations performed to evaluate the effect of scaling and fouling on HFFO membrane at two side by side FO units (set-up # 1 and set-up # 2).

1

2 **2.3 Chemicals**3 **2.3.1. DS and FS**

4 KCl and NaCl were used as DS. To assess the effect of DS on scaling, KCl was initially used
5 in 1, 2 and 3 M concentrations for baseline tests and the flux was evaluated separately against
6 deionized (DI) water as FS and specific organic foulant loaded DI water as FS, respectively.
7 Based on the results, further studies for the inorganic scaling and organic fouling were made
8 with 2 M KCl DS. FSs, which have various brackish ground water (BGW) qualities
9 representing total dissolved solids (TDS) of 5, 10, 20 and 35 g/L, were prepared from
10 different analytical grade chemicals and reported as B5, B10, B20 and B35, respectively.
11 NaCl, Na₂SO₄, CaCl₂·2H₂O, MgCl₂·6H₂O, NaHCO₃ and KCl reagents (supplied by Chem-
12 supply, Australia) were used to prepare various BGW qualities FS and their constituent
13 details are summarized in **Table 1**. These synthetic BGW represent water samples at various
14 salt interception scheme locations in Murray Darling Basins of Australia. All FS and other
15 DS were prepared by dissolving respective salts into DI water. DI water was also used as FS
16 for baseline (reference line) tests.

17

1

2 Table 1 Detailed composition of various synthetic BGW qualities evaluated for the FO
3 fouling study. Osmotic pressure (π , atm) was calculated using OLI Stream Analyser 3.2
4 software.

Compounds/Concentration	B5	B10	B20	B35
	mmol	mmol	mmol	mmol
NaCl	31.8	63.5	127.1	222.5
Na ₂ SO ₄	6.3	12.6	25.3	44.2
KCl	0.9	1.8	3.6	6.3
CaCl ₂ .2H ₂ O	1.1	2.2	4.3	7.6
MgCl ₂ .6H ₂ O	9.7	19.4	38.8	68
NaHCO ₃	0.6	1.1	2.3	3.9
π (atm)	2.74	5.35	10.56	18.56

5

6 2.3.2. Organic foulants

7 Three different model organic foulants were used to evaluate their fouling potential on FO
8 membrane: sodium alginate (Sigma-Aldrich), being polysaccharides that constitute a major
9 fraction of soluble microbial products in wastewater (Mi and Elimelech, 2010), BSA being
10 proteins and amino acids, and HA (Sigma-Aldrich) being natural organic carbon (NOC)
11 produced by biodegradation of dead organic matter. Alginate represents the hydrophilic
12 fraction of organic foulants and the molecular weight of sodium alginate ranges from 12 to 80
13 kDa. Other characteristics of alginate can be found elsewhere (Jin et al., 2012). Alginate is
14 negatively charged within the fouling study pH range (6–8) (Wang et al., 2010). Humic

1 substances are refractory anionic macromolecules and consist of both aromatic and aliphatic
2 components primarily with phenolic and carboxylic functional groups.
3 For each of these model foulants, a stock solution was prepared by separately mixing 2.4 g of
4 individual foulants in 1 L of DI water. Alginate and BSA (received in powder form) were
5 dissolved in DI water and mixing was continued for 24 h to ensure complete dissolution. HA
6 stock solution was prepared by dissolving HA powder in DI water and adjusting the pH to 8.2
7 with 0.01N NaOH. The HA stock solution was mixed continuously for 24 h to ensure
8 complete dissolution and then stored in amber glass bottles at 4 °C for further use. FS used in
9 fouling studies was individual foulants and following combinations: HA+Alginate,
10 HA+BSA, Alginate+BSA, and HA+Alginate+BSA. These model foulants were used in 60
11 mg/L each concentration to prepare various FS qualities.

12

13 **2.4 Water flux measurement**

14 Water flux was evaluated by continuously measuring the loss of FS tank weight placed on a
15 digital weighing scale (Model: CUW 4200H by CAS, Korea), which was directly connected
16 to a computer. It was recorded every 1 min. FO experiments were carried out for 4–10 h
17 based on targeted evaluation of the FO membrane for scaling or organic fouling. Some
18 experiments were run for up to 36 h for long time operations.

19

20 **2.5 Performance checks**

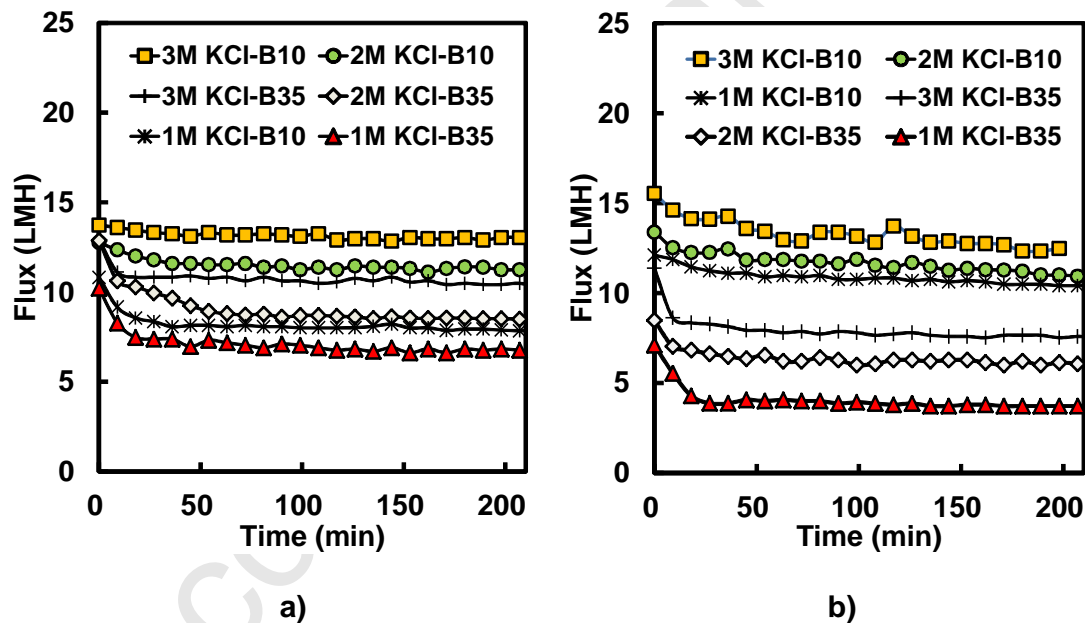
21 At the end of each fouling test, as indicated in **Fig. 2**, performance checks were carried out
22 for all membranes with 2 M NaCl as DS and DI water as feed. After the fouling experiment a
23 normal flush (using Re of 1900 and 700 on FS and DS side, respectively) was done with 1 L
24 of DI water to gently remove any additional DS/FS solutes from the membrane and FO
25 module was moved to set-up # 1. The performance of the fouled FO membrane was initially

1 evaluated with 2M NaCl DS against DI water FS using the existing FO fouling evaluation
2 approach and later with the new Tahir approach.

3 3. Results and discussion

4 3.1. Influence of FS and DS concentration on flux behaviour

5 FO was initially evaluated using set-up # 1 with 2 M NaCl as DS and DI water as FS in both
6 AL-FS and AL-DS membrane orientations. Baseline flux was also obtained. After baseline
7 tests, HFFO modules were shifted to set up # 2 and FO was operated for 1, 2 and 3 M KCl as
8 DS and various BGW quality FS (B5, B10, B20 and B35) for AL-FS and AL-DS.
9



10

11

12 Fig. 3 Effect of changing FS (for inorganic fouling) and DS concentration on HFFO flux a)
13 in AL-FS and b) AL-DS.

14

15 3.1.1 Flux behaviour in AL-FS orientation

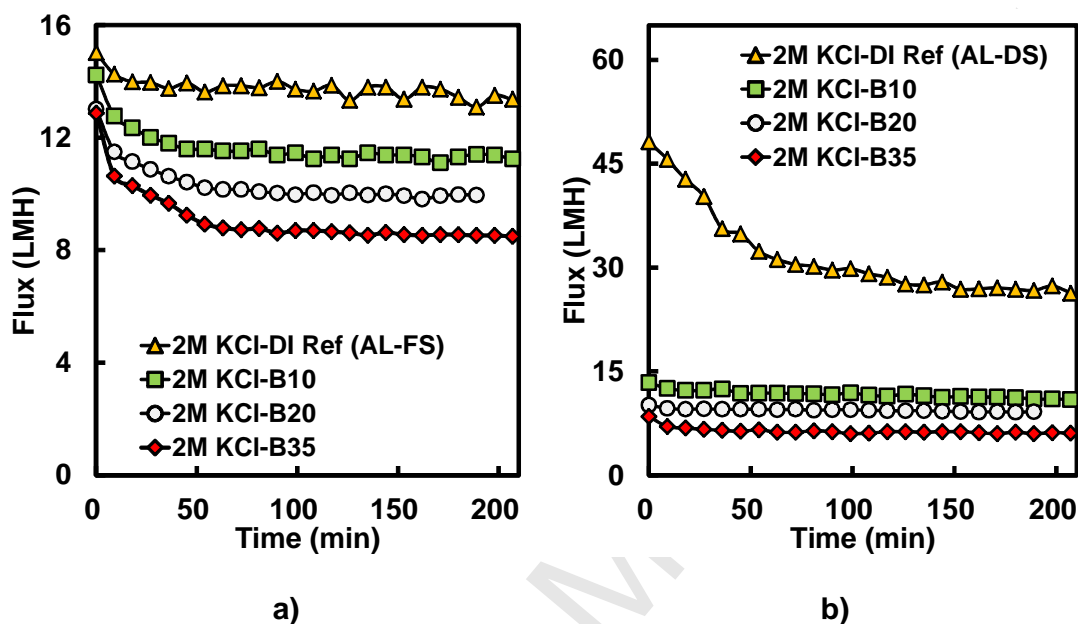
16 Fig. 3(a) presents the flux outcomes for AL-FS orientation when the HFFO was evaluated for
17 two different FS concentrations (B10 and B35) with various DS concentrations of 1–3 M

1 KCl. It was observed that the flux inconsistently changed by the change in FS and DS
2 concentrations. With the changing DS concentration, water flux increased with the increase in
3 osmotic pressure of the DS, nevertheless; the increase of experimental flux was non-linear
4 with the changes in DS concentration (Phuntsho et al., 2013, Lotfi et al., 2015). Results
5 indicated that, for an increase of DS concentration from 1 and 3 M KCl, the flux increased by
6 32% for B10 FS, whereas for B35 FS, it showed a flux increase of 26%. However, the flux
7 reduced by 8 % for 1 M KCl DS and 14% for 3 M KCl DS when FS quality was increased
8 from B10 to B35. The flux curves for various DS and FS concentrations behaved differently
9 and showed two distinct performance ranges along the test run. In all cases, the flux declined
10 rapidly in the initial 30 min followed by a steady state flux level. For 1 M KCl DS, the flux
11 changed by 21–28% for various FS concentrations in the initial 30 min, whereas the flux
12 changes by only 3–8% in the 30–200 min. These results indicated that, during the initial
13 period, DS and FS built ICP and ECP interactions on the AL and SL of the membrane and
14 this affected the flux outcome. Further, the observed flux changes during the initial period
15 were higher than the apparent effect of possible DS dilution and FS concentration with time.
16 For this reason, it is suggested that, during the initial experimental time, the higher flux
17 decline was due to the strong interactions between the solute particles and membrane surfaces
18 that helped ICP/ECP build up and rapidly reduced the flux. Later, as the development of FS
19 and DS solute's association reached the cusp, the build-up became uniform and the flux
20 changed in the remaining test run only appear to be due to the subsequent dilution of the DS
21 and the concentration of the FS side. To confirm this hypothesis, a few experiments were run
22 for 36 h, but no serious change was observed in the flux patterns.

23

24 **3.1.2 Flux behaviour in AL–DS orientation**

1 FO performances were further evaluated in AL–DS membrane orientation using the same
2 experiment protocols. The 1-3 M KCl was used as DS against B5, B10, B20 and B35 as FS,
3 and the resultant flux variation is presented in **Fig. 3(b)**. It should be noted that the flux
4 curves for these DS and FS combinations showed a different order from the AL–FS
5 orientation, which indicated that the ICP and ECP build-up differently at AL–FS and AL–DS
6 membrane orientations. Similar to the AL–FS membrane orientation, the flux patterns
7 showed two distinct parts, with the flux declined quickly in the initial test time followed by
8 gradual decline for DS dilution. However, in the AL–DS orientation, the flux reduced quickly
9 in a shorter time of 20 min and the flux-declining trend became nearly linear. The flux curve
10 at the later stage indicated insignificant flux changes in FO operations because the driving
11 force did not change remarkably with the changes in DS dilution and FS concentration.

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6 Fig. 4 Effect of changes in FS concentration on FO flux a) for AL-FS and b) for AL-DS
7 membrane orientation.

8

9 3.2 Effect of inorganic FS concentration on flux behaviour

10 Based on the flux patterns in earlier tests using various DS concentrations, 2 M KCl DS was
11 selected for rest of the study. Baseline water flux was first evaluated with 2 M KCl DS
12 against DI (Reference), B10, B20 and B35 quality FS (**Fig. 4**). FO in the AL-FS orientation
13 showed a flux drop of only 12% as the flux declined from 15.02 LMH to 14.23 LMH when
14 the FS concentration was changed from DI water to 10 g/L BGW (**Fig. 4(a)**). However, for
15 AL-DS orientation, FO initially showed a sharp decline in water flux as the FS concentration
16 was changed from DI water to B10, B20 and B35. The water flux dropped from 48.2 LMH to
17 12.7 LMH indicating a flux drop of 73% when FS concentration was changed from DI water
18 to B10 (**Fig. 4(b)**). Later, for the changes in the FS concentration of B10 to B20 (10 g/L) did

17

1 not produce similar effect as flux declined by 9.95% and 20% for AL–FS and AL–DS
2 orientation, respectively.

3

4 Earlier studies have shown that the flux decline is attributed to the enhanced ICP/ECP effect
5 developed by the high FS concentrations (Suh and Lee, 2013, Tang et al., 2010, McCutcheon
6 et al., 2006, McCutcheon and Elimelech, 2006). For higher FS concentration, ECP
7 development begins as water permeation starts from FS to DS. As the pure water permeate
8 through the membrane, depending upon the FO membrane orientation, the FS solute
9 enrichment increases at the FS and AL or SL interface. This enhanced FS solute
10 concentration causes a reduction of the net effective osmotic pressure difference for the FO
11 process and as a result, a resultant lower FO flux output is derived. However, the flux
12 outcome for the AL–DS membrane orientation (**Fig. 4(b)**) indicated that the flux declined
13 immediately from the start of the experiment, before the FS solutes concentration could start
14 to rise due to water permeation towards DS. This indicated that apart from the possible ICP
15 and ECP effects, some other forces, developed with the possible association of FS and the
16 membrane surface material, also played a significant role for the drastic reduction of water
17 flux in AL–DS orientation. It is suggested that the divalent FS solutes components, such as
18 Ca^{2+} and Mg^{2+} , developed additional interactions with the functional groups of the membrane
19 SL or at the SL–AL interface were mainly responsible for the water permeation through
20 osmosis. The rapid flux changing phenomena may be further attributed to the SL pore
21 blocked by FS solutes (Majeed et al., 2013). These outcomes stressed the need for further
22 studies in this area to track membrane functional groups influencing FO flux outcome for
23 changes in FS concentration.

24

1 To check the effect of fouling on FO membrane, few membrane modules were alternatively
2 collected after 20 min of fouling tests, gently rinsed and placed on FO setup # 2. The
3 membrane performance was checked using 2 M NaCl DS and DI water FS. All of these
4 membranes showed performances similar to baseline (within $\pm 2.12\%$ range). Results
5 indicated that the initial flux declines shown in **Fig. 3 and 4** were not due to fouling, but to
6 some interactions between FS solutes and AL or SL of the membrane.

7

8 **3.3 Effect of organic foulants on FO flux performances**

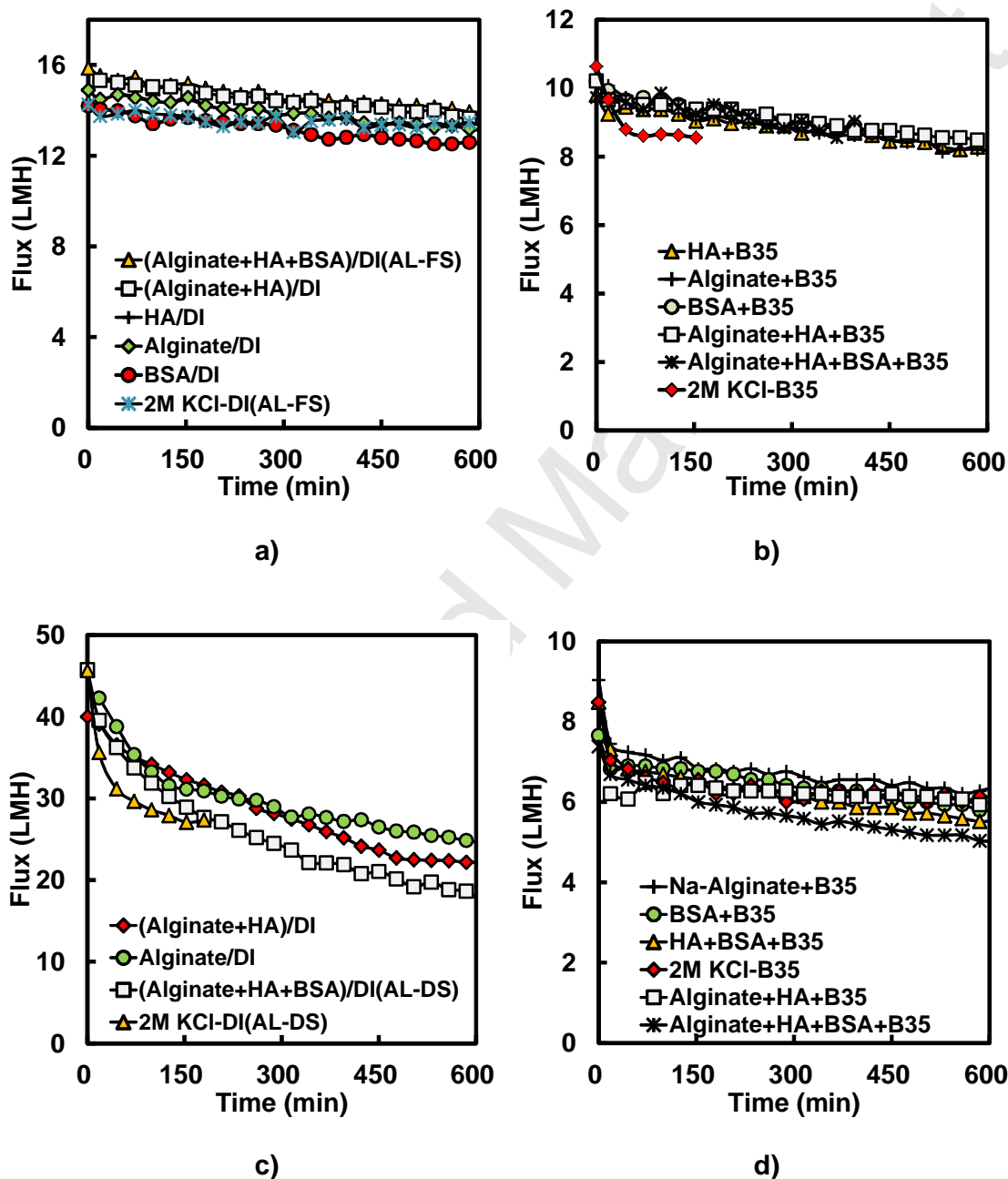
9 Three model foulants, such as alginate, HA and BSA were studied to investigate the effect of
10 organic fouling on the FO process. The 2 M KCl was used as DS for these experiments.
11 Alginate, HA and BSA were initially evaluated in individual concentrations of 60 mg/L with
12 DI water FS for organic fouling potential. Later FO was also tested with all possible
13 combination of 60 mg/L each of alginate, HA and BSA with varying BGW FS concentrations
14 to assess the synergic effect of organic foulants and FS solutes on FO performances.

15

16 **3.3.1 Flux performance in AL–FS orientation**

17 **Fig. 5** illustrates the effect of alginate, HA and BSA on flux when the FO was operated at
18 AL–FS orientation using DI water and B35 FS. It was observed that FO showed higher flux
19 with FS carrying alginate, HA and BSA in DI water than DI water DS (**Fig. 5(a)**). Compared
20 to 2 M KCl DS and DI water FS baseline, the FS carrying each of alginate, HA and BSA in
21 DI water even showed 5.6% higher flux outcome (**Fig. 5(a)**). Foulants build-up on the FO
22 membrane increased the negative charges of the membrane surface and resulted a higher flux
23 outcome (Tiraferri and Elimelech, 2012). The results also indicated that once the fouling
24 layer started to develop on the FO membrane surface, the net ionic charges and the functional
25 groups of these foulants facilitated the permeation of water molecules. This further confirmed

1 that, compared to pressure driven processes, FO in AL-FS orientation shown more stability
 2 in flux and this result was in good agreement with the earlier findings (Tang et al., 2010,
 3 Achilli et al., 2009).



8 Fig. 5 Effect of model organic foulants on flux performance of FO process with a) DI water
 9 FS in AL-FS; b) B35 in AL-FS; c) DI water FS in AL-DS; and d) B35 in AL-DS orientation.

1 2M KCl was used as DS for both AL-FS and AL-DS orientation, crossflow Reynolds
2 number for FS and DS were 1900 and 700, respectively and temperature was 25 ± 0.5 °C.

3 **Fig. 5(b)** also showed a similar trend when alginate, HA and BSA were used with B35 FS.
4 After 30 min of operation, FS carrying organic foulants showed a 9.11% higher flux than that
5 of the B35 FS. Interactions between the foulant species and membrane surface helped the
6 negative charges on the membrane surface to rise, which enhanced the flux through the
7 membrane. Divalent Ca^{2+} and Mg^{2+} ions also attached to negatively charged fouling layers
8 but did not show their effect on flux reduction.

9

10 3.3.2 Flux performance in AL-DS orientation

11 **Figs. 5 (c) and (d)** further show the performance of the HFFO membrane in the AL-DS
12 orientation for various organic foulants and the changing FS qualities. **Fig. 5(c)** represents the
13 flux outcome when HFFO was operated with various combinations of alginate, HA and BSA
14 in DI water FS. It was found that, in comparison to FO operations in AL-FS, the flux is
15 affected with model foulants in varying order. In contrary to the results in AL-FS orientation,
16 the FS carrying combined (alginate + HA + BSA) foulants did not show a higher flux in AL-
17 DS orientation, while the FS loaded with alginate/HA showed a higher flux. FS carrying only
18 alginate initially showed a lower flux, followed by a higher flux after 300 min of operation.

19

20 FO flux was evaluated in AL-DS orientation for B35 FS carrying organic foulant and the
21 results are presented in **Fig 5(d)**. Similar to **Fig. 4(b)**, FO showed a very low flux when
22 operated for organic foulant loaded B35 FS. Organic foulants with B35 FS showed a similar
23 flux behaviour as shown with the DI water FS. Alginate carrying FS showed a higher flux
24 whereas alginate/HA/BSA loaded FS showed a lower flux outcome. These outcomes
25 indicated that the developing fouling layers played an important role for the changes of FO

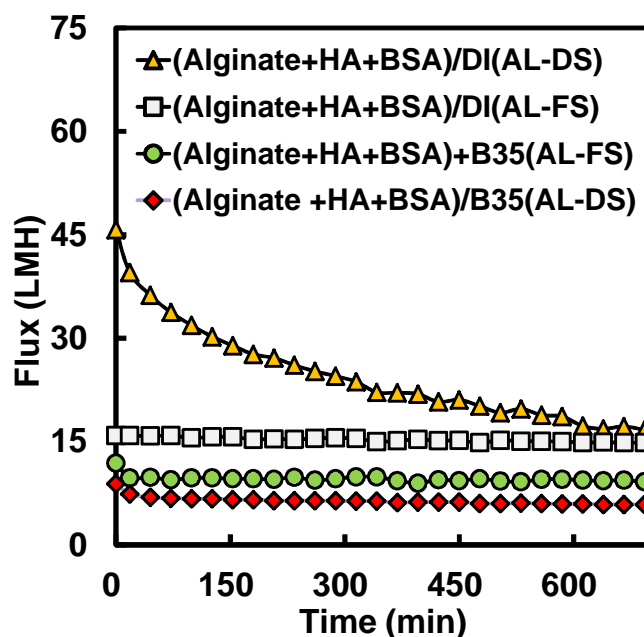
1 performance. Initially, the fouling layer association with the membrane modify the osmotic
2 behaviour of the membrane and resulted flux increase. Later, it supports pore-blocking
3 phenomena to reduce flux performances of the membrane. **Fig. 5** shows that the water flux in
4 both the AL-FS and AL-DS membrane orientation enhanced slightly with the development of
5 the organic foulant layer. **Figs. 5 (c) and (d)** further indicated that, for AL-DS orientation,
6 FS carrying foulants drastically reduced the flux outcome possibly due to the induced severe
7 internal clogging on the SL. It was different from the AL-FS orientation, where fouling
8 phenomena was dominated by cake layer formation on the relatively smooth rejection layer
9 (Mi and Elimelech, 2010).

10

11 During the fouling process, the organic and particulate matter accumulates inside the porous
12 structure of the support layer and reduces membrane permeability. Reverse salt flux can be
13 built up in the support layer and reduce the effective osmotic driving force (Cath et al., 2013).
14 These results further indicated that the water flux loss due to fouling on the FO membrane
15 was collectively caused by a combination of (1) the physical blocking of the active pores
16 associated with the AL or SL structure by the FS components; 2) enhanced concentrative ICP
17 which reduced the mass transfer coefficient of the SL; 3) internal clogging in the support
18 structure of the FO membrane which likely reduced the porosity and mass transfer rate,
19 enhancing the structural parameter which resulted in additional hydraulic resistance; and 4)
20 the enhanced CP development in the attached fouling layer [30]. The impact of initial fouling
21 layer on flux behaviour can mainly be attributed to pore plugging and CP effects at the AL
22 and SL of the membrane. Later attachments of the new layers to the initial fouling layer did
23 not enhance this combination effect.

24

1



2

3 Fig. 6 Effect of membrane orientation and FS concentration on FO flux. Conditions: DS=
 4 2M KCl, FS=DI and BGW35 carrying alginate, HA and BSA were used in 60 mg/L
 5 concentration each. Membrane orientation: evaluated for both AL-FS and AL-DS,
 6 temperature = 25 ± 0.5 °C.

7

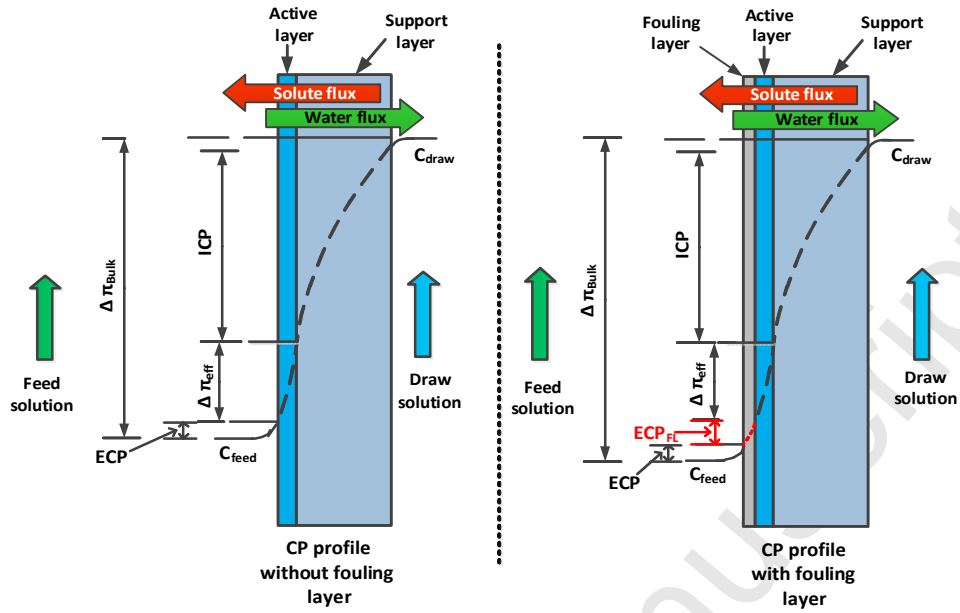
8 **Fig. 6** illustrates the effect of membrane orientation and the combined effect of inorganic and
 9 organic components of the FS on HFFO membrane flux. Paralleling the earlier results for
 10 BGW FS outcome as shown in **Fig. 4**, for alginate/HA/BSA loaded FS with DI, the HFFO
 11 membrane showed high flux in AL-DS orientation whereas the FO showed the lowest flux
 12 for alginate/HA/BSA loaded FS with B35. These results reflected the serious pore blocking
 13 and CP affected by the FS carrying inorganic solutes which restricted the flux outcomes in
 14 AL-DS orientation (Majeed et al., 2015). The higher flux outcome with organically fouled
 15 membrane indicated that higher negative charged of the FO membrane helped to facilitate the
 16 quick and easy penetration of water molecules. It further indicated that the water permeation

1 through membrane starts with the association of the positively charged (H^+) part of water
2 molecule with the negatively charged sites of the membrane functional groups. These
3 associations facilitated water molecules to come closer and passed quickly through the
4 membrane pores.

5

6 These results further indicated that depending on the type of membrane orientation, newly
7 formed fouling layer on the FO membrane produced different CP effects. It provided an extra
8 thick layer on either the AL or SL of the membrane and resulted additional ICP or ECP build-
9 up on FO membrane and affected FO flux. **Fig. 7** shows the varying effect of ICP and ECP
10 on FO membrane due to the newly developed fouling layer. For the developed fouling layer
11 on FO membrane, ECP showed higher effects on flux in AL-FS than ICP effects on AL-DS
12 orientation. The thickness of the fouling layer also helped to enhance the ICP effects which
13 reduced the flux attributed to cake layer formation (Mi and Elimelech, 2008). These results
14 suggested that the higher portion of the flux decline for FO fouling in AL-DS was caused by
15 the pore blocking or cake enhanced resistance, whereas for AL-FS, the CP resistance mainly
16 contributed to a flux drop.

17

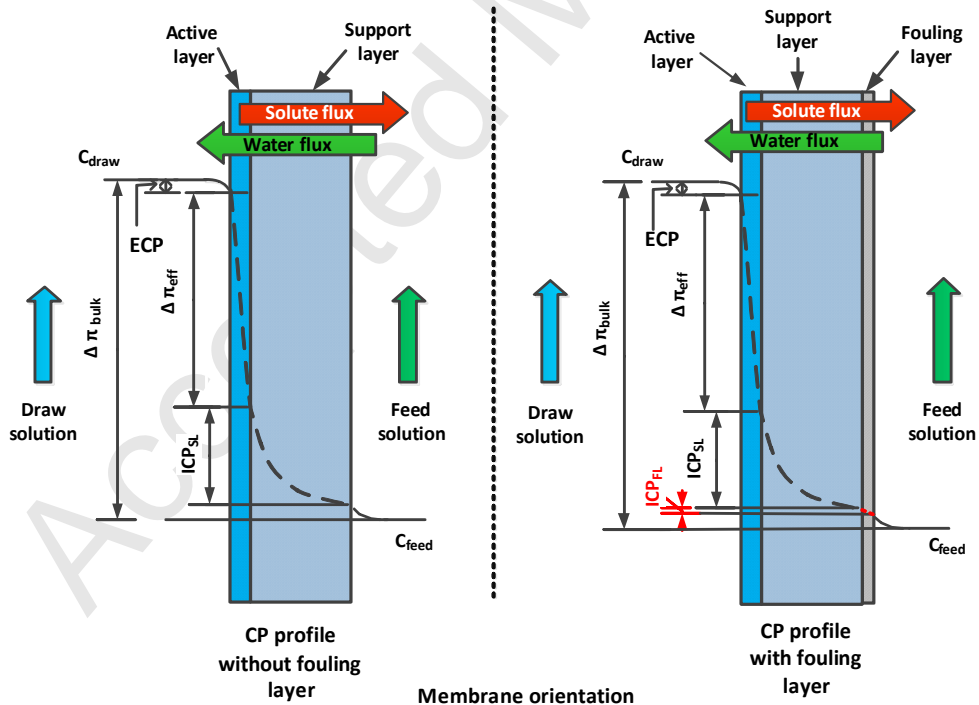


Membrane orientation
Active layer facing FS (AL-FS)

1

2

a)



Membrane orientation
Active layer facing DS (AL-DS)

3

4

b)

1 Fig. 7 Effects of fouling layer on the ICP and ECP for FO operations a) at AL–FS and b) at
2 AL–DS.

3 **Figs. 4 and 5** have already indicated that when DS and FS qualities are changed, the flux
4 does not change linearly to reflect the changes in the osmotic pressure difference. Some
5 portion of the osmotic pressure increase is offset by the possible changes in the ICP/ECP
6 effects (**Fig. 7**). For higher DS concentrations, the effectiveness of the net osmotic pressure
7 decreases with the higher concentrations of FS. CP quickly builds-up with high BGW solute
8 concentration in FS and this results in a lowering of the net osmotic pressure at the membrane
9 interface (Majeed et al., 2015). For this reason, difference of flux outcome increases more at
10 high FS concentration.

11

12 **3.4. Delusion behind the scaling and fouling approach for hollow fiber forward osmosis** 13 **membrane**

14 **Figs. 3-6** presented flux behaviour for HFFO membrane using FS carrying BGW and organic
15 foulants. Apparently all curves directed reducing flux trends and indicated occurrence of
16 possible fouling phenomena. Following the existing fouling approach, these fouling
17 judgements were made by comparing any flux curve behaviour with the baseline curve at any
18 particular time and the difference between these two points was referred as to fouling effect.
19 These fouling observations were made considering the presence of constant driving force
20 acting on FO process, thus Figs. 3-6 indicated significant differences in the flux for fouling,
21 and however, the actual fouling potential seems different from the apparent one.

22

23 Opposite to RO/NF/MF/UF systems, the changes in the FO driving forces are extremely
24 dynamic as they continuously affect the FO flux performance. Multiple flux driving forces
25 simultaneously act on FO, which do not remain fixed during the FO operation rather keep

1 changing constantly. In FO, no two points show the similar driving force while comparing
2 any two FO flux curves; hence the flux outcome did not provide a reliable comparison of any
3 two such performances at any particular time. The same flux declining curves using different
4 driving forces cannot be used to ascertain the fouling potential on the FO membrane surface
5 for any DS and FS. Hence, from the existing methodology of FO flux data curve comparison,
6 it is difficult to find how much of the flux is affected individually by the changing driving
7 forces and the fouling and scaling or ICP/ECP issues (**Fig. 1**). For these reasons, the standard
8 flux curves comparison for FO operation, may not be reasonably used for evaluating the
9 fouling potential of the FO membrane.

10

11 To accommodate the issue of constantly changing flux-driving forces for FO fouling as
12 summarized in **Fig. 1**, Tahir approach is used ahead to evaluate the fouling risk for FO
13 process. To check the absolute effect of FO fouling on the flux performance, the FO
14 membrane was initially evaluated at FO set-up # 1 with a different DS (2 M NaCl) and DI
15 water FS and the baseline flux was recorded for an average 10 min of test run. FO fouling
16 experiments were conducted on set-up # 2 for specific DS (2 M KCl) and varying FS
17 concentration carrying different combinations of BGW and organic foulants (**Fig. 2**). On
18 completion of each fouling test run, a 10 min slow rinsing with DI water was carried out on
19 both sides to remove excessive DS and FS from the fouling experiment. The module is then
20 moved to set-up # 1 and the FO was evaluated for the same initial driving force using 2 M
21 NaCl DS and DI water FS to indicate any changes in the FO membrane flux performance.
22 The average of the initial 10 min flux was evaluated to compare the membrane performances.

23

24 **3.4.1 Real effects of inorganic fouling on FO performances**

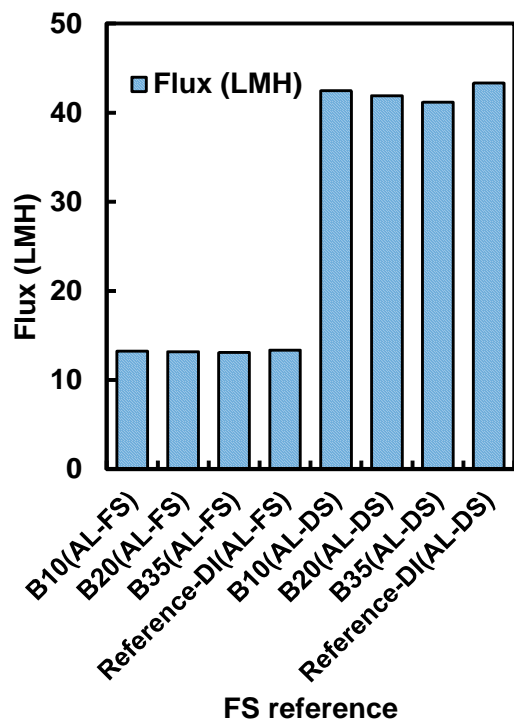
1 Using the experimental protocol outlined in **Fig. 2** for Tahir fouling approach, the water flux
2 was monitored for HFFO membrane in AL-FS and the AL-DS orientations and results are
3 presented in **Fig. 8**. The results indicated that the FO flux performance was barely affected by
4 the changing BGW FS quality. FO in AL-FS orientation showed a smaller flux decline than
5 in the AL-DS orientation. For B35 FS, the results showed that the HFFO flux declined by
6 0.25 LMH (3%) in AL-FS orientation. However, in AL-DS orientation, up to a 2.16 LMH
7 (5.6%) flux drop was observed for similar FS (**Fig. 8(a)**).

8

9 **Fig. 8(b)** showed the flux outcome for step-1 and step-5 following Tahir fouling protocol
10 where the FO was operated for 2 M KCl DS and B35 FS in both AL-FS and AL-DS
11 membrane orientations. Results show that, in AL-FS orientation, for a longer test run with
12 B35 FS, the FO flux dropped by 0.38 LMH (2.64%), which indicated a minimal effect in
13 terms of fouling. However, HFFO showed a higher flux decline of 2.59 LMH (5.92%) when
14 operated in AL-DS membrane orientation. These results were different from the results
15 presented above in **Figs. 4 and 5**, which failed to clearly indicate fouling effect for various
16 DS and FS combinations as they shown flux behaviour influenced by various forces. Thus it
17 did not demonstrate real flux changes specifically for scaling.

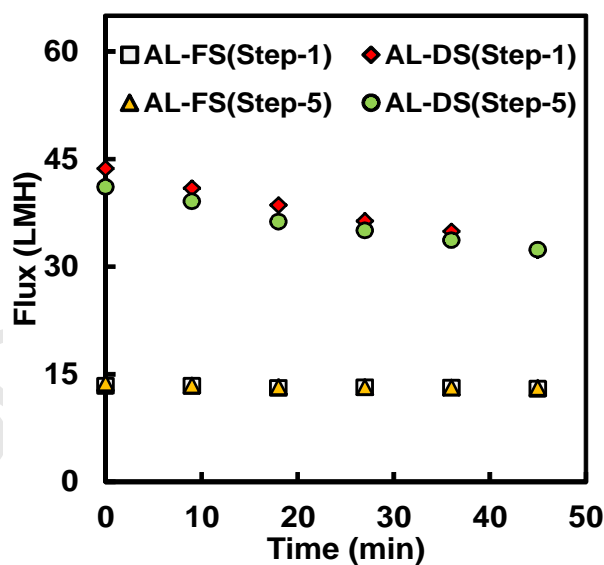
18

19



FS reference

a)



b)

1
23
4

5 Fig. 8 Effect of scaling on HFFO membrane performance: a) for AL-FS and AL-DS
 6 membrane orientation with 2 M KCl DS and B10, B20 and B35 as FS, b) flux performance
 7 for step-1 and step-5. 2 M KCl was used as DS against B35 FS for both AL-FS and AL-DS
 8 membrane orientation, Temp=25 ± 0.5 °C.

1

2 **3.4.2 Real Effect of combined fouling on HFFO performances**

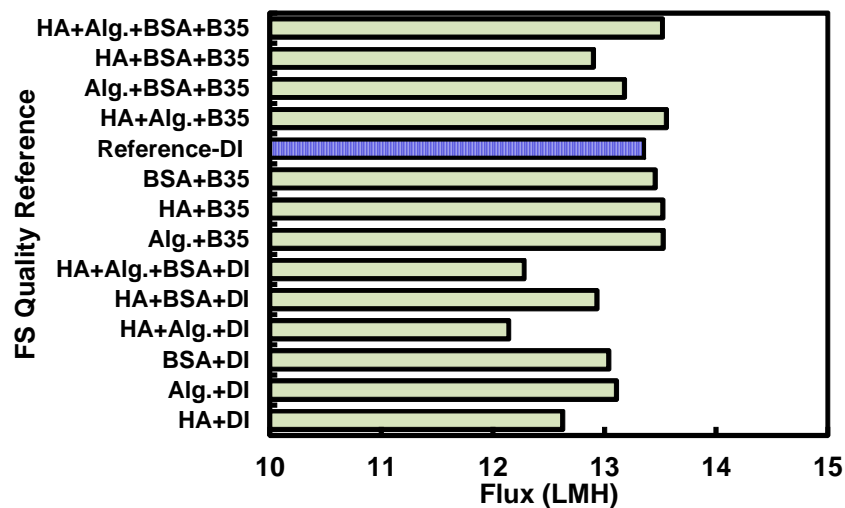
3 Following the **Fig. 2** experimental protocol, the HFFO was evaluated for fouling issues using
4 2 M KCl DS and DI water and B35 FS carrying alginate, HA and BSA and results were
5 summarized in **Fig. 9**. **Fig. 9(a)** presented the performance of the FO membrane when
6 operated at AL–FS orientation. The outcomes showed varying fouling effect for FO in
7 relation to different FS. The results indicated higher fouling for the HFFO membrane for
8 organic foulants/DI water FS than organic foulants/ BGW FS. Flux with FS carrying 60 mg/L
9 each of HA and Alginate in DI dropped to 12.18 LMH indicating a flux drop of up to 9% due
10 to fouling. On the other hands, when used with B35, they showed little flux decline. FO
11 indicated lower fouling potential for organic foulants/BGW FS. A flux drop of up to 4% was
12 also observed for B35 FS carrying 60 mg/L each of HA and BSA.

13

14 Different fouling effects with similar FS and DS for AL-FS and AL-DS membrane
15 orientation suggest that apart from effects of the membrane properties and foulant
16 characteristics, flux potential is also driven by some other forces. In the current design of
17 HFFO module, similar cross flow velocity indicated varying Re flow within and outer side of
18 lumens and exerts varying shear force. High crossflow shear forces resist fouling layer
19 development process by overcoming the foulant-membrane attractive forces. The crossflow
20 shear force acting within the HF lumen does not allow any fouling layer development and
21 reduces the HFFO fouling risk for AL-FS orientation. Further, any foulant attached to inner
22 lumen surface is easily pushed out by the sheer force generated by the crossflow velocity
23 especially for FS flowing through the fiber lumens (**Fig. 10**). Hence, in AL–FS orientation,
24 little or no flux loss was observed with the combined fouled FS. Lower fouling results with

1 B35 indicates that the bridging of divalent Ca^{2+} and Mg^{2+} ions with the foulants functional
 2 groups depressed the adhesion potential of the fouling layer.

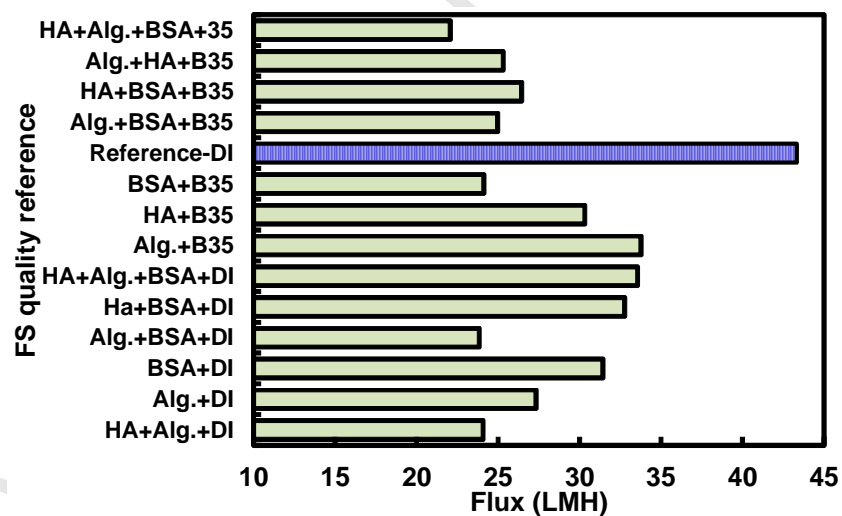
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4

5

a)



6

7

b)

8 Fig. 9 Effect of the combine organic fouling on the performances of HFFO membrane a) flux
 9 in AL-FS membrane orientation b) flux in AL-DS membrane orientation.

10

11

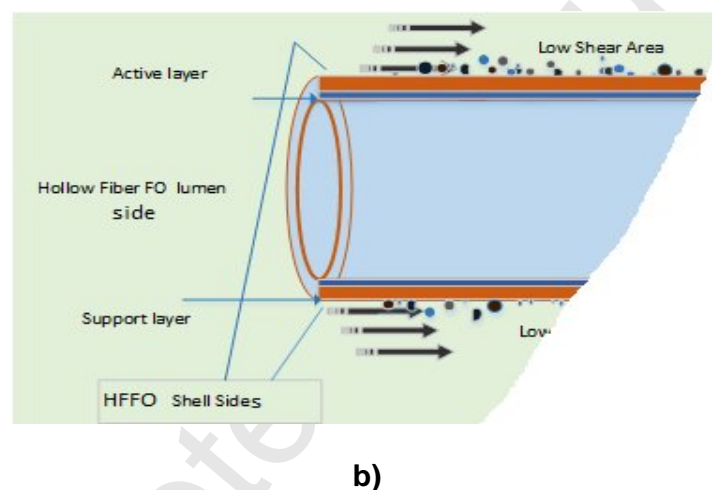
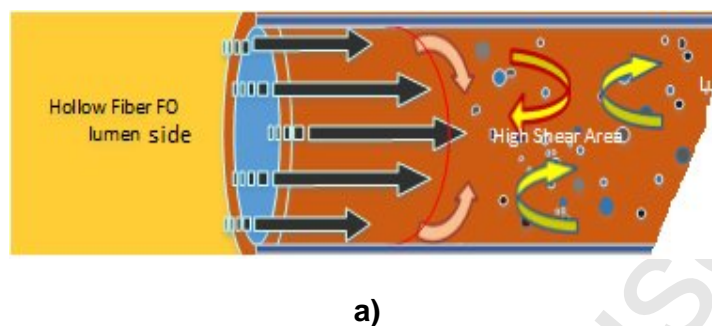
1 Furthermore, when FO was evaluated in AL–DS orientation using alginate, HA and BSA
2 foulants in DI water and BGW FS, the flux dropped by 16–49%, indicated high fouling risk
3 for HFFO membrane at AL–DS (**Fig. 9(b)**). Similar to AL–FS orientation, FO in AL–DS
4 orientation also indicated high fouling for FS carrying organic foulants in DI water. However,
5 for few cases, it showed high fouling with BGW FS. B35 DS carrying 60 mg/L each of HA,
6 alginate and BSA foulants showed high fouling and indicated a flux drop of 49% for fouling.
7 The lower flux outcomes indicated that, in AL–DS orientation, the FO membrane is highly
8 prone to a greater risk of fouling. Among the three model foulants, the BSA loaded FS
9 showed much apparent flux decline than HA and alginate.

10

11 The observed differences in the fouling rate at different membrane orientations reflected the
12 influence of varying associations among the foulants and surface charge, hydrophilicity and
13 zeta potential of the associated layers of the FO membrane influenced by the flow shear
14 forces. These results also suggested that the different flow shear forces acting on FO seem
15 primarily responsible for varying fouling behaviour for AL–FS and AL–DS membrane
16 orientations. **Fig. 10** indicated the consequences of DS and FS streams flowing with varying
17 Re through the HFFO membrane for scale development and deposition. In AL–FS membrane
18 orientation, FS passed through HFFO lumens. The given FS crossflow rate produced a high
19 shear force inside of the HF lumens, generating swirling movements that left fewer
20 opportunities for scale build-up on inner surface of the FO lumens. Thus, a lower flux decline
21 was observed for AL–FS orientation. Higher cross-flow velocity led to reduction of
22 aggregation of the feed solids to form the fouling layer. The sheer force turbulence overcame
23 the membrane–foulants interaction force and avoid fouling layer development on the
24 membrane surface in AL–FS orientation. Reduced hydrophobicity and increased electrostatic

1 repulsion led to a lower deposition rate of these foulants onto the membrane surface and thus
 2 less fouling (Hong and Elimelech, 1997).

3



8 Fig. 10 Graphical presentation for effects of varying crossflow shear forces within and
 9 outside HFFO lumens affecting fouling behaviours of HFFO membrane in a) AL-FS and b)
 10 AL-DS orientation.

11

12 On the contrary, due to the HFFO module design issues, the similar working crossflow rate
 13 was unable to deliver the similar swirling effect on the HF outer surface. The feeble shear
 14 force left a more favourable environment for the deposits build-up and results comparatively
 15 higher flux drop in the AL-DS membrane orientation.

16

1 **Figs. 4-6** indicated fouling using existing methodology for FO fouling whereas **Figs. 8 and 9**
2 showed FO fouling potential using Tahir approach. Comparing the FO performance curves
3 presented in **Figs. 4-6** with **Figs. 8 and 9** for two different fouling evaluation approaches, it
4 can be seen that the results presented by the existing approach showed a better flux outcome
5 or less fouling for alginate, HA and BSA loaded FS. This stood true for AL-FS but indicated
6 misleading outcome for AL-DS orientation. These comparisons further indicated that for the
7 FO process, as the existing fouling approach did not indicate true fouling risks for FO
8 membranes rather directed toward misleading outcome, it may not be used effectively to
9 identify the real fouling issues for the FO membrane. This comparison highlighted the severe
10 interference of the interacted forces with the FO performance especially in relation to internal
11 concentration polarization (ICP)/external concentration polarization (ECP). The effect of
12 possible ICP and ECP intensification with fouling layer growth on FO membrane was still
13 unclear, however, the possibilities in relation to the ICP and ECP intensification of the
14 fouling layer should not be ruled out.

15

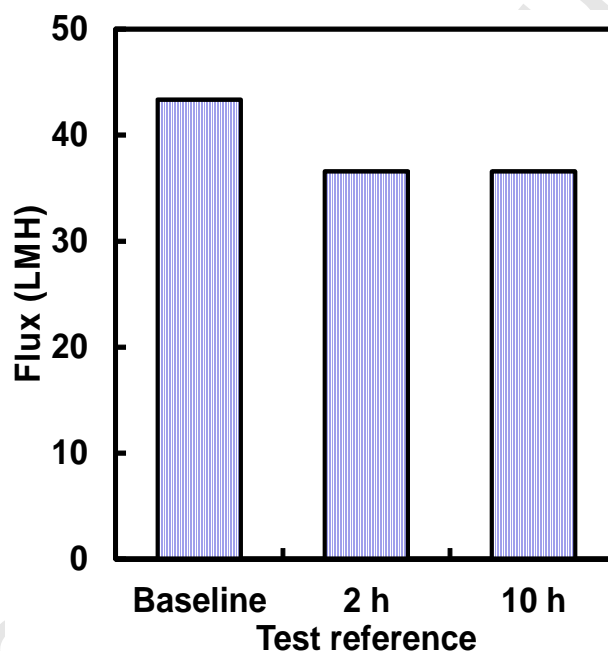
16 **3.5 Fouling development process during FO combined fouling**

17 The development of fouling on FO membrane was also assessed with reference to the
18 duration of the operation. FO was evaluated in AL-DS orientation for FS carrying 60 mg/L
19 each of alginate, HA and BSA in DI water and 2 M KCl DS for a period of 2 and 10 h
20 separately. At the end of experiments, resultant flux was also evaluated on FO set-up # 1 and
21 the flux performance was recorded. The results shown nearly similar flux of 36.58 LMH and
22 36.56 LMH for the two tests operated for 2 and 10 h respectively (**Fig. 11**), indicated a flux
23 loss of about 18% due to HFFO fouling. The similar flux outcomes for FO membrane
24 operated for different times indicated that the fouling layer on the FO membrane developed
25 during the initial stage of FO test run contributing to the reduction in the FO flux

1 performance. This also indicated that the initial fouling layer blocked the membrane pores,
2 which mainly affected flux for the membrane process. The later deposition of the other
3 fouling layer seemed loose which did not appear to contribute to the further plugging of
4 membrane pore. Accordingly, no or lower flux decline was observed with subsequent fouling
5 for longer FO test run. More detailed studies are required to further evaluate how these FS
6 characteristics affect the FO flux driving force at the initial stages.

7

8



9

10 Fig. 11 Fouling development progress with time (AL-DS)

11

12 FO showed mixed flux trends with all model organic foulants evaluated in this study. The
13 formation of a cross-linked gel layer is also observed when the FO was operated in AL-DS
14 orientation for alginate, HA and BSA loaded FS (**Fig. 12**). These prominent and easily
15 distinguishable fouling layers are observed in all experiments using FS carrying dark brown

- 1 coloured HA. This fouling layer is found firmly stuck to the membrane surface and found
- 2 really hard to separate it from the membrane outer surface by vigorous shaking.
- 3

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1

2



3

4

5 Fig. 12 Fouling layer developed on HFFO lumen fiber module used for a) AL-FS and b)
6 AL-DS respectively

7

8 **4. Conclusions**

9 The HFFO membrane was evaluated to investigate the effects of fouling for two different
10 fouling evaluation protocols using various BGW FS qualities carrying model organic foulants
11 such as alginate, HA and BSA. The following conclusions are drawn from the outcomes of
12 this study:

- 13 • An immediate flux drop at AL-DS orientation in a very short time test run does not
14 follow the existing CP concept. This indicates role of possible associations between
15 the FS solutes and active and support layer of FO membrane. These cause a drop in
16 the net osmotic pressure at the membrane interface and resultant flux outcome, which
17 is independent of the general CP. This reduced flux may not be classified as either
18 scaling or fouling.

- 1 • Due to continuous changes in FO driving force and their associated effects on flux
2 outcome, the fouling effects for FO cannot be worked out using routine FO fouling
3 experimental approaches used similar to RO/NF/MF/UF.
- 4 • The fouling process for FO is reviewed and an alternative approach is suggested to
5 evaluate the actual loss of the FO flux due to scaling and fouling which successfully
6 shown the real impact of the fouling on the FO flux.
- 7 • It is found that paralleling other membrane systems, the HFFO membrane also carries
8 nearly the same risk for fouling, however, the crossflow rates leave different results
9 for FO fouling in AL-F and AL-DS orientation.
- 10 • The respective influence of foulants on the FO flux is different for both the AL-FS
11 and AL-DS membrane orientation. HFFO showed a higher fouling risk at AL-DS
12 orientation.
- 13 • The crossflow rate seems to play an important role for varying fouling outcomes for
14 the HFFO membrane in both the AL-DS and AL-FS membrane orientation. Further
15 studies may easily lead to some adjustments in the appropriate process conditions for
16 effective fouling control in FO process.

17

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22

1

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