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1 **Sulfur-containing air pollutants as draw solution for fertilizer drawn forward**  
2 **osmosis desalination process for irrigation use**

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11 **Abstract**

12 This study investigated suitability and performance of the sulfur-based seed solution (SBSS)  
13 as a draw solution (DS), a byproduct taken from the photoelectrochemical (PEC) process  
14 where the SBSS is used as an electrolyte for H<sub>2</sub> production. This SBSS DS is composed of a  
15 mixture of ammonium sulfate ((NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>) and ammonium sulfite ((NH<sub>4</sub>)<sub>2</sub>SO<sub>3</sub>), and it can be  
16 utilized as fertilizer for fertilizer drawn forward osmosis (FDFO) desalination of saline water.  
17 The FDFO process employed with thin-film composite (TFC) membrane and showed that the  
18 process performance (i.e. water flux and reverse salt flux) is better than that with cellulose  
19 triacetate (CTA) membrane. In addition, it produced high water flux of 19 LMH using SBSS as  
20 DS at equivalent concentration at 1 M and 5 g/L NaCl of feed solution (model saline water).  
21 Experimental results showed that the reverse salt flux of SBSS increased with the increase in  
22 pH of the DS and that lowering the concentration of ammonium sulfite in the SBSS led to the  
23 higher water flux of feed solution. The result also demonstrated that this SBSS is practically

- 24 suitable for the FDFO process toward development of water-energy-food nexus technology
- 25 using sulfur chemicals-containing air pollutant.
- 26 **Keywords:** By-product solution; Forward osmosis; Desalination; Draw solution; Fertilizer;
- 27 Fertigation.

## 28 1 Introduction

29 The world's population is growing rapidly and so are the issues related to fresh water, food  
30 and energy significantly affecting the global economies [1, 2]. Among three elements in the  
31 energy-water-food nexus, water is perhaps the most essential part for enhancing agriculture's  
32 productivity and hence global food security. Agriculture sector uses over 70% of the world's  
33 total fresh water consumption [3]. Nevertheless, water stress has been a severe issue for  
34 decades in many regions in our planet. The impact of climate change is further worsening the  
35 water stress such as through unpredictable rainfall events, extreme weather conditions and  
36 frequent drought [4-6].

37 Many attempts have been made to develop technologies and water management policies to  
38 combat water issues by using alternatives such as impaired water and unlimited saline water  
39 resources [2]. Desalination is one of the most reliable technologies for augmentation of  
40 limited fresh water sources [2]. While desalination is used for potable water supplies including  
41 for some industrial applications, it is still not a viable option for irrigation where the water  
42 requirement is huge. Currently available desalination technologies including reverse osmosis  
43 (RO) and thermal based processes are high capital and energy intensive [7-10] albeit  
44 significant improvement in membrane and energy efficiency has been made in the last few  
45 decades. Since energy, water and environment issues are all interconnected [9, 10], it is vitally  
46 important for any desalination technology to have significantly lower energy consumption  
47 especially for large-scale irrigation purpose. For arid countries such as Qatar, Australia where  
48 there is abundant of brackish groundwater in the inland areas and seawater along the coastal  
49 areas, the availability and wide-range application of low cost desalination technologies might  
50 have substantial impacts on agriculture sector.

51 Forward osmosis (FO) has recently emerged as a novel process for various applications  
52 including for desalination. FO process is driven by the natural osmotic process without the  
53 need of high hydraulic pressure as for the RO process and hence the power consumption of  
54 FO process itself is much lower than the RO process although they use similar salt rejecting  
55 membranes [9, 11-15]. In FO process, the main driving force is generated from the intrinsic  
56 osmotic pressure differential between the draw solution (DS) and the feed solution (FS) when  
57 separated by a semi-permeable membrane. DS plays a pivotal role in FO process since it is the  
58 primary source of net driving force across the membrane. The FO process therefore converts  
59 saline water sources into the diluted DS instead of pure water and hence post-treatment  
60 processes are necessary to obtain pure water for potable purpose. One of major challenges  
61 of the FO process however is the lack of appropriate draw solute [16]. The separation and  
62 regeneration of draw solutes from the diluted DS to obtain pure water and reuse of  
63 concentrated draw solute is complex which not only requires additional process but also  
64 requires significant energy. The ease and efficiency of DS recovery and separation will be the  
65 primary factors for the success of FO desalination in the future for portable applications [17].  
66 However, if desalinated water can be put into use directly without the need for separation  
67 and regeneration of DS, FO has considerable advantage over RO desalination technology.  
68 Several small-scale applications have been developed based on this concept such as hydration  
69 bags for nutritious drinks useful in emergencies or in the boats [18].  
70 However, one of the most practical and novel applications of the FO process is in the  
71 desalination for irrigation purpose using concentrated fertilizers as DS. The diluted fertilizer  
72 DS can be used directly for fertigation without recovery and regeneration of DS. This fertilizer  
73 drawn forward osmosis (FDFO) desalination process [16, 19] can use any commercially  
74 available soluble fertilizers as DS to produce high osmotic pressures that is able to extract

75 pure water from the FS having low osmotic pressure. As the fertilizer nutrients are essential  
76 for plants, the need for draw solute separation and regeneration is avoided and hence saving  
77 energy for post-treatment [20]. Recently, the application of FDFO process has been examined  
78 for the desalination of brackish groundwater [20] and seawater [16, 19] with promising results  
79 that FDFO can be extensively applied for fertigation.

80 With this vein, this study has explored to find appropriate DS to meet the global demand for  
81 sufficient food supply with less water usage and low energy consumption for fertigation under  
82 the category of development of water-energy-food nexus technology. Here, we used sulfur-  
83 containing chemical solutions that can be made by sulfur-containing air pollutants (e.g., SO<sub>2</sub>).  
84 One of the major air polluting gases released from the thermal power plants is the sulfur  
85 dioxide (SO<sub>2</sub>). In the past decades, a huge amount of SO<sub>2</sub> is emitted into the atmosphere  
86 because of the increasing rate of burning the coal and other fossil fuel for energy [21]. The  
87 emission of SO<sub>2</sub> has resulted in serious environmental problems, such as acid rain and fine  
88 particles that can have a significant impact on the human health and the environment. There  
89 have been many in-situ pretreatment methods widely employed to lessen the emission of  
90 these polluting gases and to protect the global environment. Among these methods, SO<sub>2</sub> has  
91 been captured to produce wallboard (gypsum) [22, 23], sulfuric acid and fertilizer [24].  
92 Recently, Han and his colleagues [25] have proposed a new method to remove SO<sub>2</sub> and  
93 simultaneously produce renewable and clean hydrogen energy. A sulfur-based seed solution  
94 (SBSS) is made of byproduct of ammonia-based desulfurization process or purging SO<sub>2</sub> into  
95 alkaline-based (sodium hydroxide) solution. Consequently, removal of SO<sub>2</sub> in this SBSS  
96 solution occurs using a photoelectrochemical (PEC) process. In this PEC process, water  
97 molecules are split into oxygen and hydrogen gases under sunlight. This technology is  
98 considered one of the most advanced technologies to produce renewable and clean

99 hydrogen. The experimental results from a study done by Han and his colleagues showed a  
100 very high removal (more than 97%) of SO<sub>2</sub> and successful production of hydrogen energy,  
101 simultaneously [25].

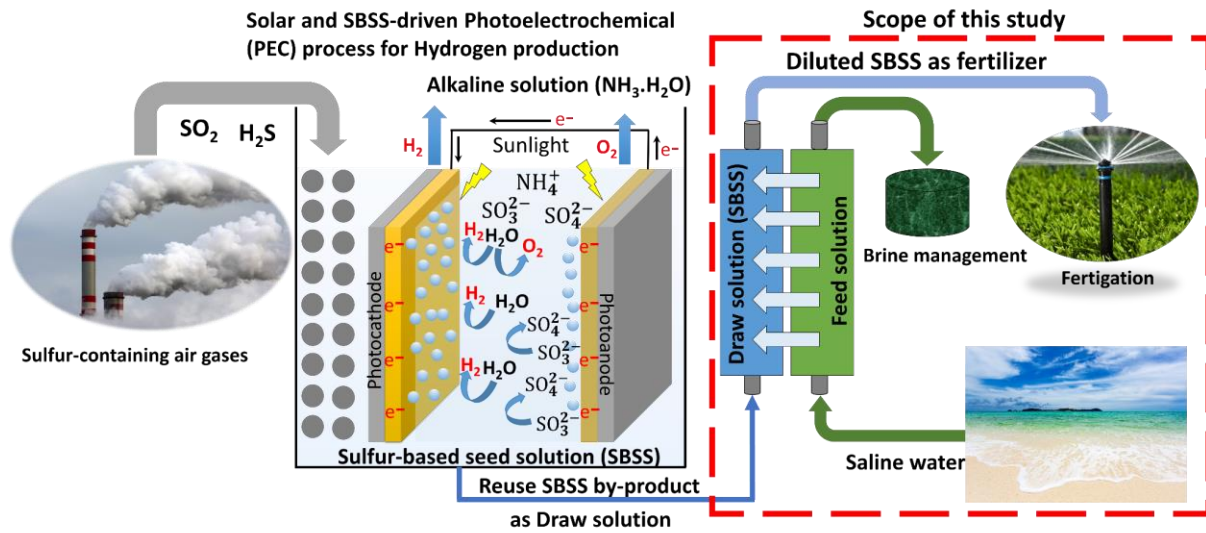
102 There are two main compounds formed at gas-dissolution reactor of ammonia-based  
103 desulfurization process when SO<sub>2</sub> is dissolved into ammonia-based solution are ammonium  
104 sulfate (SOA - (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>), and ammonium sulfite (SIOA - (NH<sub>4</sub>)<sub>2</sub>SO<sub>3</sub>). The solution can then be  
105 employed for the PEC system. SIOA can also be oxidized to SOA during PEC process:



107 PEC water splitting process works as a concentrating process where SBSS is gradually  
108 concentrated, therefore, SBSS after going through PEC system, becomes highly concentrated  
109 (>2 mol/L) [26], meaning it can create high osmotic pressure and can be used in FDFO  
110 desalination process. It is highly likely that the composition of SOA and SIOA may vary during  
111 the H<sub>2</sub> production by the PEC system or the FO process. While SOA is a commonly used  
112 fertilizer and found that SOA is one of the most suitable fertilizers for FDFO desalination [16,  
113 27], the performance of the SIOA has not studied yet. It is therefore important to understand  
114 how this might affect the performance of the FDFO desalination process.

115 As these two advanced technologies (PEC water splitting process and FDFO) have been proved  
116 to be compromising ones, the concept of this research is integrating the production of  
117 renewable and clean hydrogen energy and water for food production.

118 The main objective of this study is to evaluate the feasibility of using SBSS – a by-product from  
119 PEC process as a fertilizer DS for the desalination of saline water by FDFO process for  
120 irrigation. The study examines the effect of SBSS on FDFO desalination of saline water by using  
121 SBSS draw solutions containing different ratios of SOA and SIOA.



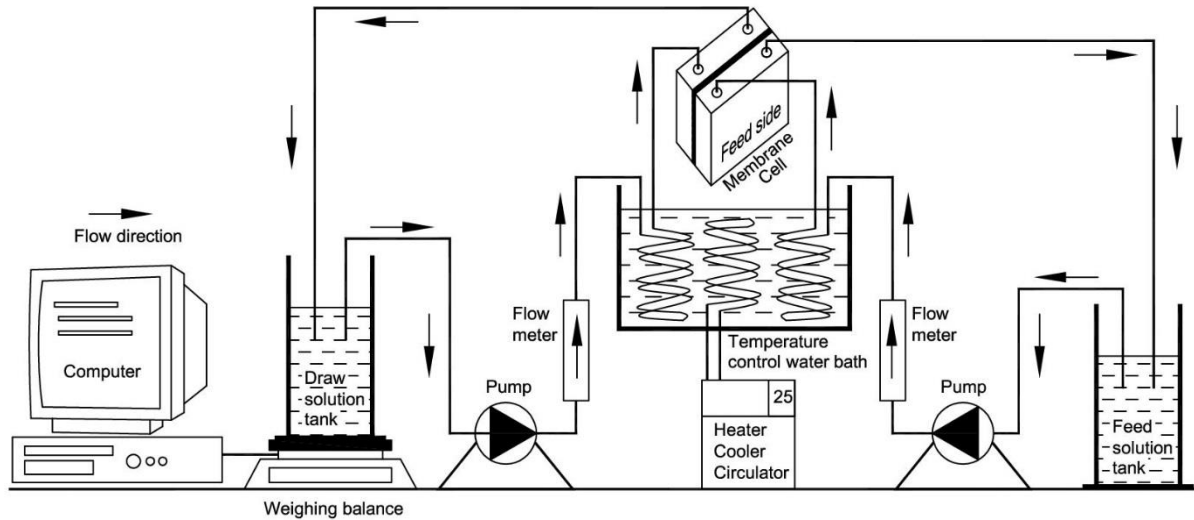
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123 Figure 1. Overall concept of using sulfur-based seed solution (SBSS) for PEC process and DFD  
 124 desalination of saline water and red-dashed line indicates the scope of the current study.



125 **2 Materials and methods**

126 **2.1 Forward osmosis experimental set up**



127

128 Figure 2. Experimental FO set up

129

130 This current study used a bench-scale FO set up (Figure 2), similar to the one used in the  
131 earlier studies [16]. The cross-flow membrane unit consists of an FO cell with channels sizes  
132 (77 mm length x 26 mm width x 3 mm depth) on both sides of the membrane to allow feed  
133 water to flow on active side of the membrane and draw solution on the support side of the  
134 membrane. Two types of commercial FO membranes were used in the experimental studies:  
135 cellulose triacetate (CTA) and thin-film composite (TFC) polyamide supplied by Hydro  
136 Technologies Inc (HTI) and Toray Industries, Inc (Toray) respectively. Two variable speed gear  
137 pumps (Cole Palmer model 75211-15, 50-5000 RPM and 0.07 HP, Thermo Fisher Scientific,  
138 USA) were used for providing crossflows (8.5 cm/s) of the feed and draw solutions at both  
139 maintained at 25°C using temperature control system.

140 2.2 *Chemicals and reagents*

141 Table 1 shows properties of chemicals used in this study. They were reagent grade supplied  
142 by Sigma-Andrich Co. LLC, Australia and used directly as received. Draw solutions and model  
143 brackish groundwater and seawater were prepared by dissolving chemicals in deionized (DI)  
144 water.

145 Table 1 Details of chemical used in this study

Name of chemical	Chemical formula	MW	Purity (%)	Supplier
Ammonium sulfate	$(\text{NH}_4)_2\text{SO}_4$	132.16	98%	Sigma-
Ammonium sulfite monohydrate	$(\text{NH}_4)_2\text{SO}_3 \cdot \text{H}_2\text{O}$	134.16	92%	Andrich
Sodium chloride	NaCl	58.44	98%	Co. LLC, Australia

146 2.3 *Calculation of draw solutions osmotic pressure and speciation*

147 In this study, different SBSS DSs were prepared by varying the composition of (SOA) and  
148 (SIOA). Osmotic pressure and speciation of these different SBSS DSs were then calculated by  
149 using OLI Stream Analyzer 9.3 (OLI Systems Inc., Morris Plains, NJ, USA) and tabulated in Table  
150 2.

151

152 Table 2 Different SBSS draw solutions and their thermodynamic properties as analysed using  
 153 OLI Stream Analyzer 9.3. S1 refers to ammonium sulfate (SOA) -  $(\text{NH}_4)_2\text{SO}_4$ , S2 refers to  
 154 ammonium sulfite (SIOA) -  $(\text{NH}_4)_2\text{SO}_3$ ; B1 – B4 refers to SBSS DSs containing different ratios of  
 155 SOA and SIOA.

SBSS DSs	Chemical composition	pH @ 1 M	$\pi$ @ 1 M (bar)	Major species formed in 1 M solution at 25°C and at 1 atm pressure		
				Major species	Concentration (M)	Diffusivity ( $10^{-9} \text{ m}^2/\text{s}$ )
S1	1 M SOA	5.15	46.75	$\text{NH}_4^+$	1.52	1.61
				$\text{SO}_4^{2-}$	0.52	0.88
				$\text{NH}_4\text{SO}_4^-$	0.48	0.83
B1	0.8 M SOA + 0.2 M SIOA	7.35	46.24	$\text{NH}_4^+$	1.62	1.63
				$\text{SO}_4^{2-}$	0.43	0.89
				$\text{NH}_4\text{SO}_4^-$	0.37	0.8
				$\text{SO}_3^{2-}$	0.19	0.80
B2	0.6 M SOA + 0.4 M SIOA	7.5	45.4	$\text{NH}_4^+$	1.72	1.65
				$\text{SO}_3^{2-}$	0.39	0.81
				$\text{SO}_4^{2-}$	0.33	0.9
				$\text{NH}_4\text{SO}_4^-$	0.26	0.86
				$\text{HSO}_3^-$	0.012	1.12
				$\text{NH}_3$	0.012	1.87
B3	0.4 M SOA + 0.6 M SIOA	7.59	44.36	$\text{NH}_4^+$	1.81	1.67
				$\text{SO}_3^{2-}$	0.58	0.83
				$\text{SO}_4^{2-}$	0.23	0.92
				$\text{NH}_4\text{SO}_4^-$	0.17	0.87
				$\text{HSO}_3^-$	0.014	1.14
				$\text{NH}_3$	0.014	1.91
B4	0.2 M SOA + 0.8 M SIOA	7.65	43.13	$\text{NH}_4^+$	1.9	1.71
				$\text{SO}_3^{2-}$	0.78	0.85
				$\text{SO}_4^{2-}$	0.12	0.94
				$\text{NH}_4\text{SO}_4^-$	0.083	0.9
				$\text{HSO}_3^-$	0.016	1.17
				$\text{NH}_3$	0.016	1.96
S2	1 M SIOA	7.7	41.76	$\text{NH}_4^+$	1.98	1.75
				$\text{SO}_3^{2-}$	0.98	0.88
				$\text{HSO}_3^-$	0.017	1.2
				$\text{NH}_3$	0.017	2.02

## 157 2.4 Determination of FO membrane transport parameters

158 Two membranes (CTA and TFC) utilized in this study were firstly characterized to determine  
159 the pure water permeability coefficient ( $A$ ) following a protocol proposed by Tiraferri et al.  
160 [28]. A laboratory-scale crossflow FO unit as described in the earlier section was used for  
161 determination of  $A$  value.

## 162 2.5 Performance measurements

163 In order to investigate the performance of FDFO process, experiments were conducted using  
164 SBSS as DS having concentrations equivalent to 1 M. To simulate the likely variations of the  
165 SBSS components in the real desulfurization plants, SBSS DS were prepared containing  
166 different SOA and SIOA ratios as described on Table 2.

167 The FS consisted of DI water and model saline water of different concentrations of total  
168 dissolved solids (TDS) prepared using NaCl. The performances of each SBSS DS were studied  
169 using the same FO membranes that were used in water permeability test.

170 Each performance experiment was operated for a duration of 8 hours. The performance of  
171 the SBSS as DS was evaluated in terms of water flux and reverse solute flux (RSF). Water flux  
172 was directly measured using digital mass balance (Nimbus Precision Balances: NBL 4602e,  
173 ADAM Equipment, USA). The balance is directly connected to a computer for online data  
174 logging at 5-minute intervals. When DI water was used as FS, RSF was monitored by measuring

175 the TDS of the FS at the end of each experiment. When model brackish water was used as FS,  
176 the RSF values were determined by analyzing the feed water samples for the presence of  
177  $\text{NH}_4^+$ ;  $\text{SO}_4^{2-}$  and  $\text{SO}_3^{2-}$  after each experiment. Collected solution samples were analyzed using  
178 Spectroquant – Merck Millipore Nova 60. As concentration of feed solutes in the sample is  
179 high compared to draw solutes, samples were diluted at several dilution factors.

180 The reverse solute flux of individual solute ( $J_S$ ) is controlled by concentration gradient  
181 between feed solution and draw solution and can be experimentally calculated as follows:

$$182 \quad J_S = \frac{(V_i - \Delta V) \times C_S}{A_m \times t} \quad (1)$$

183 where,  $V_i$  is the initial volume of FS,  $\Delta V$  is the total volume of pure water that permeates to  
184 the DS from the FS,  $C_S$  is the concentration of draw solutes in the FS at the end of experiment,  
185 and  $A_m$  is the membrane area ( $m^2$ ), while  $t$  is the experiment duration (hour).

186 The experimental water fluxes were then calculated using following equation:

$$187 \quad J_w = \frac{\Delta V}{A_m \times t} \quad (2)$$

188 where  $\Delta V$  is the total volume difference of DS between initial volume and volume at the end  
189 of each experiment,  $A_m$  is the membrane area ( $m^2$ ), and  $t$  is duration of experiment (in this  
190 study,  $t = 8$  hours).

191

192 It is essential to use a ratio of RSF to water flux termed as specific reverse solute flux (SRSF)  
193 in evaluating performance of draw solutes. SRSF indicates that the amount of draw solutes  
194 reversely diffuse to FS per unit volume of water extracted from the FS [18]. SRSF can be  
195 determined by the following equation:

$$196 \quad SRSF = \frac{J_S}{J_w} \quad (3)$$

197 The performance ratio (PR) in terms of percentage was also employed to assess the  
198 performances of the SBSS DS for FDFO desalination process. PR is the percentage ratio of  
199 experimental water flux to theoretical water flux (theoretical flux calculated based on the  
200 pure water permeability coefficient ( $A$ ) and predicted osmotic pressure from OLI software).

$$201 \quad PR (\%) = \frac{J_{wt}}{J_w} \times 100 \quad (4)$$

202 Where,  $J_{wt}$  and  $J_w$  are theoretical water flux and experimental water flux, respectively.

203 In addition, feed salt rejection is an important parameter in the FO processes. In this study,  
204 the forward rejections of the feed solutes were measured by taking DS samples at the end of  
205 experiment and analyzing it for Na<sup>+</sup> and Cl<sup>-</sup> ions by ~~inductively coupled plasma mass~~  
206 ~~spectroscopy~~ (Spectroquant – Merck Milipore Nova 60). Analyzing solution samples for  
207 specific ions proved highly challenging, especially for DS samples as the DSs concentrations  
208 used in this study were significantly higher compared to the concentration of feed solutes  
209 present in the DS samples after each experiment. The DS samples have to be diluted by several  
210 factors before samples were analysed.

211 The measurement of rejection was carried out based on the following equation:

$$212 \quad Re (\%) = \frac{C_i - \frac{C_{p,D}(V_i + \Delta V)}{\Delta V}}{C_i} \times 100 \quad (5)$$

213 where,  $C_i$  and  $C_{p,D}$  are initial concentration of ion in FS and final concentration of ion in DS,  
214 respectively.  $V_i$  is initial volume of DS, and  $\Delta V$  is the total amount of pure water permeated  
215 to DS from FS.

## 216 3 Results and discussion

217 3.1 Performance of FDFO process using CTA and TFC FO membranes, SBSS as draw  
218 solutions with DI water as feed solutions.

219

220 Table 3. Performance of SBSS as DSs in the DFDO process using DI water as FS.

SBSS DSs	pH at 1M	$\pi$ at 1 M (bar)	J <sub>wt</sub> (LMH)		J <sub>w</sub> (LMH)		PR (%)		J <sub>s</sub> (gMH)	
			CTA	TFC	CTA	TFC	CTA	TFC	CTA	TFC
S1	<a href="#">5.15</a>	46.75	54.70	76.20	11.21	19.85	20	26	4.59	4.51
B1	<a href="#">7.35</a>	46.24	54.11	75.38	10.65	21.04	20	28	7.52	4.61
B2	<a href="#">7.50</a>	45.40	53.12	74.01	10.76	21.03	20	28	7.53	6.91
B3	<a href="#">7.59</a>	44.36	51.90	72.31	10.42	21.04	20	29	7.33	5.77
B4	<a href="#">7.65</a>	43.13	50.47	70.31	10.21	20.46	20	29	8.23	5.30
S2	<a href="#">7.70</a>	41.76	48.85	68.06	10.22	18.68	21	27	8.53	5.91

221 SBSS: Sulfur-based seed solution;  $J_{wt}$ : Theoretical water flux;  $J_w$ : Experimental water flux; PR:  
 222 Performance ratio;  $J_s$ : Reverse solute flux; RSFS: Reverse solute flux selectivity is the ratio of  
 223 experimental reverse solute flux  $J_s$  to experimental water flux  $J_w$ .

224 **3.1.1 Experimental versus theoretical water fluxes of the SBSS draw solutions**

225 Theoretically, the water flux trend produced by SBSS DSs should be similar to the osmotic  
 226 pressure trend by virtue of the main driving force in FO process which is the osmotic pressure  
 227 difference between DS and FS across the membrane [29]. However, results in Table 3 shows  
 228 that only using CTA membrane is experimental water flux trend consistent to osmotic  
 229 pressure trend, while the inconsistency was seen using TFC membrane. Notably, S1 was  
 230 envisaged to achieve the highest water flux thanks to its highest osmotic pressure, but the  
 231 experimental water flux produced by this DS was the second lowest among SBSS draw  
 232 solutions. B1 and B3 achieved the highest water flux (21.04 LMH), narrowly followed by B2  
 233 and B4 with 21.03 LMH and 20.46 LMH, respectively. Concentration polarization (CP) effect  
 234 [including both external CP and internal CP](#) is probably attributed to this phenomenon and  
 235 lower solute resistance (K) inside the membrane support layer in FO mode (AL - FS)  
 236 exacerbates the severity of internal CP effect [30-32]. A DS containing high diffuse solutes will  
 237 have a low K value, hence producing higher water flux. As can be seen from the Table 2,  
 238 diffusivity of solutes in SBSS increases with the increase in concentration of SIOA.

239 In general, FDFO process performance was consistently better using TFC membrane than  
240 using CTA membrane as shown in Figure 43. When SBSS were used as draw solutions,  
241 experimental water fluxes generated by FDFO process using TFC membrane were almost  
242 twice higher (ca. 21 LMH) in comparison to using CTA membrane (ca. 11 LMH) in all pairs. The  
243 much higher water flux of the TFC membrane is predictable as TFC has higher pure water  
244 permeability ( $A = 1.63 \text{ LMHbar}^{-1}$ ) and lower structural parameter ( $S = 312 \mu\text{m}$ ) compared to  
245 the CTA membrane ( $A = 1.17 \text{ LMHbar}^{-1}$ ) and ( $S = 473 \mu\text{m}$ ). It is also because the TFC  
246 membrane is made of polyamide, which is able to achieve higher water flux and higher solute  
247 rejection in comparison to that of CTA membrane [33]. Performance ratio (PR) is also a  
248 significant parameter as it represents the percentage of bulk osmotic pressure effectively  
249 available for generating water flux in the FO process [34, 35]. Table 3 shows that using TFC FO  
250 membrane, SBSS draw solutions were consistently better at generating water flux in FDFO  
251 process. Most of SBSS draw solutions were able to obtain effective bulk osmotic pressure up  
252 to 30% using TFC membrane compared to using CTA of approximately 20%. High water flux  
253 and PR are desirable for the economic viability of the FDFO process as it reduces the total  
254 membrane area and hence the capital cost.

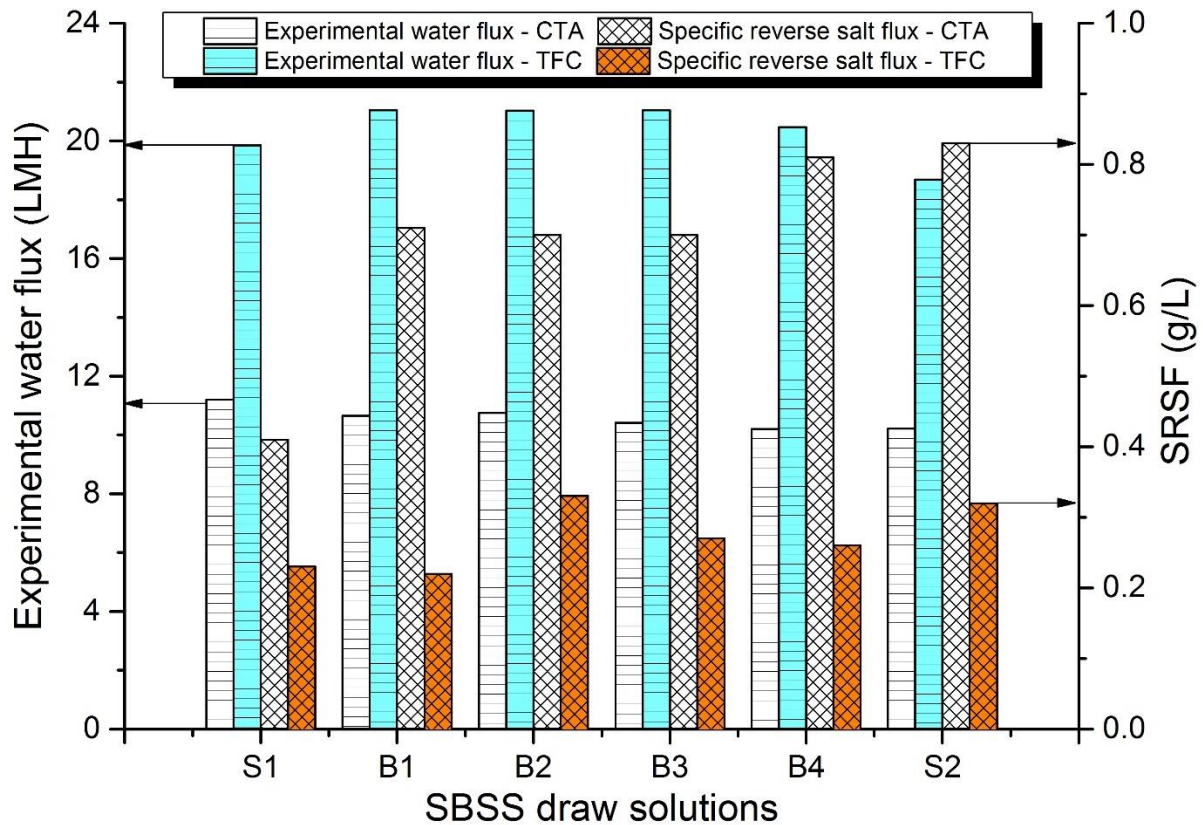
### 255 3.1.2 Reverse solute diffusivity of the SBSS draw solutions

256 The lowest SRSF for CTA membrane was observed for S1 DS (0.41 g/L) whereas with other  
257 SBSS DS, the SRSF was almost twice with 0.70, 0.71, 0.81 and 0.83 g/L for B2, B3, B1, B4 and  
258 S2, respectively. It is clear from Figure 3 that, the TFC membrane shows relatively much lower  
259 SRSF than the CTA membrane for all the DS conditions tested in this study. The SRSF for the  
260 TFC FO membrane were not significantly different from each SBSS DS showing values of 0.22,  
261 0.23, 0.26, 0.27, 0.32 and 0.33 g/L for SBSS DS B1, S1, B4, B3, S2 and B2, respectively. It is



262 commonly recognized that a FDFO process achieving higher water flux and lower SRSF is  
 263 preferred since higher SRSF might reduce the net bulk osmotic pressure of draw solutions and  
 264 cause detrimental effects for feed brine management.

265



266

267 Figure 3. Experimental water fluxes and specific reverse solute fluxes (SRSF) generated by  
 268 different SBSSs as draw solutions in FDFO process.

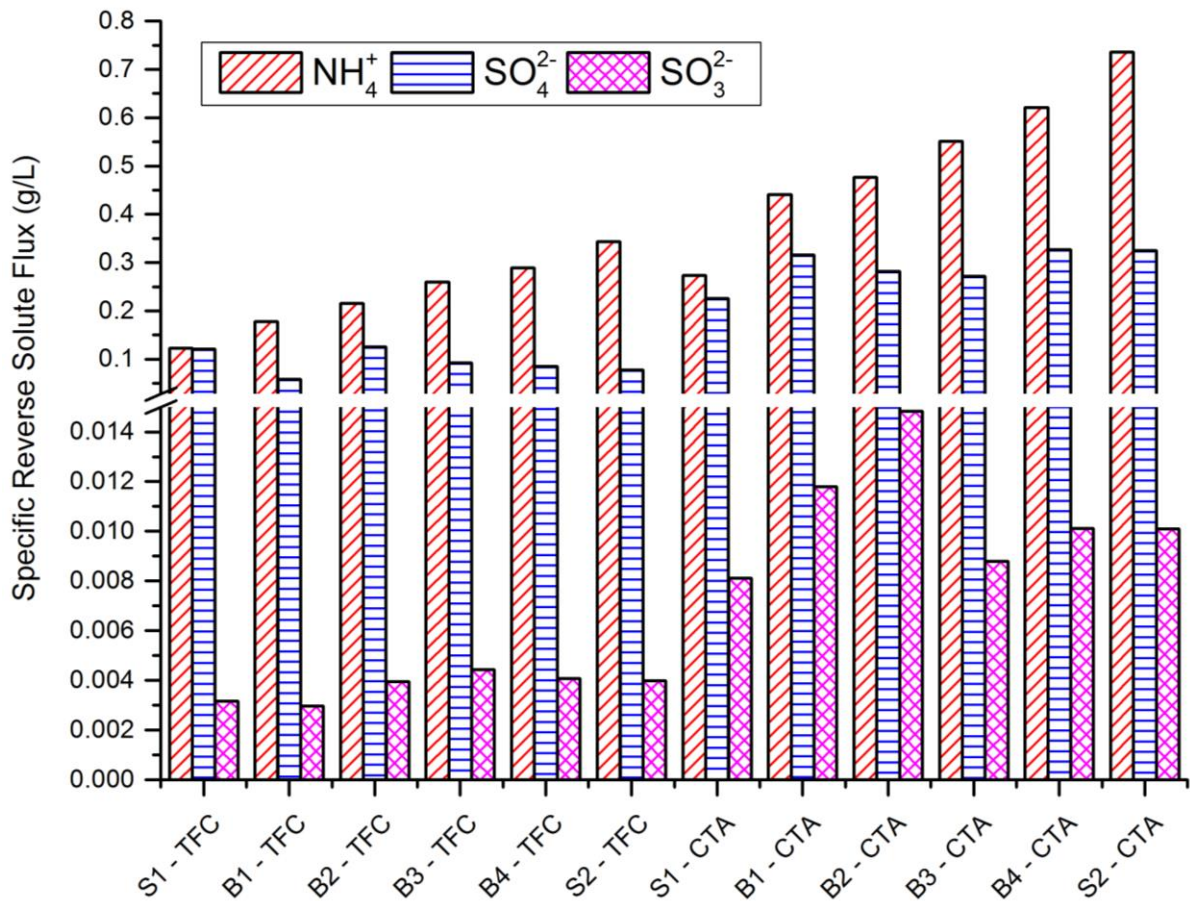
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270 Comparing the SRSF amongst the different SBSS DS, it appears to increase at higher SIOA  
 271 concentrations compared to SOA in the SBSS DS although this trend is more clearly evident  
 272 for CTA than the TFC membrane. This could probably be explained owing to the combined  
 273 effects of increased pH of DS, molecular size and diffusivities of the ions in the SBSS DS. Table  
 274 3 shows that pH of SBSS DSs increased from pH 5.15 for S1 to 7.7 for S2 with increasing SIOA  
 275 concentration. Cation transport across the FO membranes can be influenced by the solution  
 276 pH and it increases under alkaline pH environment [36]. The deprotonation of membrane

277 active layer occurs under alkaline conditions making the membranes more negatively charged  
278 for both the membranes [37, 38]. As the  $\text{NH}_4^+$  has much smaller molecular size and higher  
279 diffusivity compared to anions present in the SBSS DS, the increased negative charge of the  
280 active layer would more strongly attract the  $\text{NH}_4^+$ , likely facilitating enhanced transport of  
281 through the polyamide active layer. This could also drag in simultaneously the transport of  
282 anions such as  $\text{SO}_4^{2-}$  and  $\text{SO}_3^{2-}$  in order to maintain electrical neutrality, thereby enhancing  
283 the SRSF of the DS. As observed from Table 2, the diffusivity of  $\text{NH}_4^+$  also increases at higher  
284 SIOA concentrations in the SBSS DS, which could also contribute to enhance SRSF of the SBSS  
285 DS.

286

287 ~~Another important parameter to evaluate on how a membrane performs with certain type of~~  
288 ~~DS is to estimate the RSFS. This parameter is measured as a ratio of water flux (Jw) over the~~  
289 ~~reverse solute flux and is in fact an inverse of the SRSF. A DS with higher RSFS is preferable as~~  
290 ~~it indicates higher water extraction capacity of the FO membrane per unit mass of the draw~~  
291 ~~solute lost through reverse diffusion thereby reducing the replenishment cost of the FO~~  
292 ~~process [11]. Table 3 shows that S1 and B1 exhibited the highest RSFS of 4.56 and 4.40 L/g,~~  
293 ~~respectively among SBSS draw solutions using TFC membrane while for CTA FO membrane~~  
294 ~~the highest RSFS was observed with S1 (2.44 L/g) as DS. This indicates that S1 and B1 DSs are~~  
295 ~~able to produce the highest volume of water per gram lost draw solute.~~



296

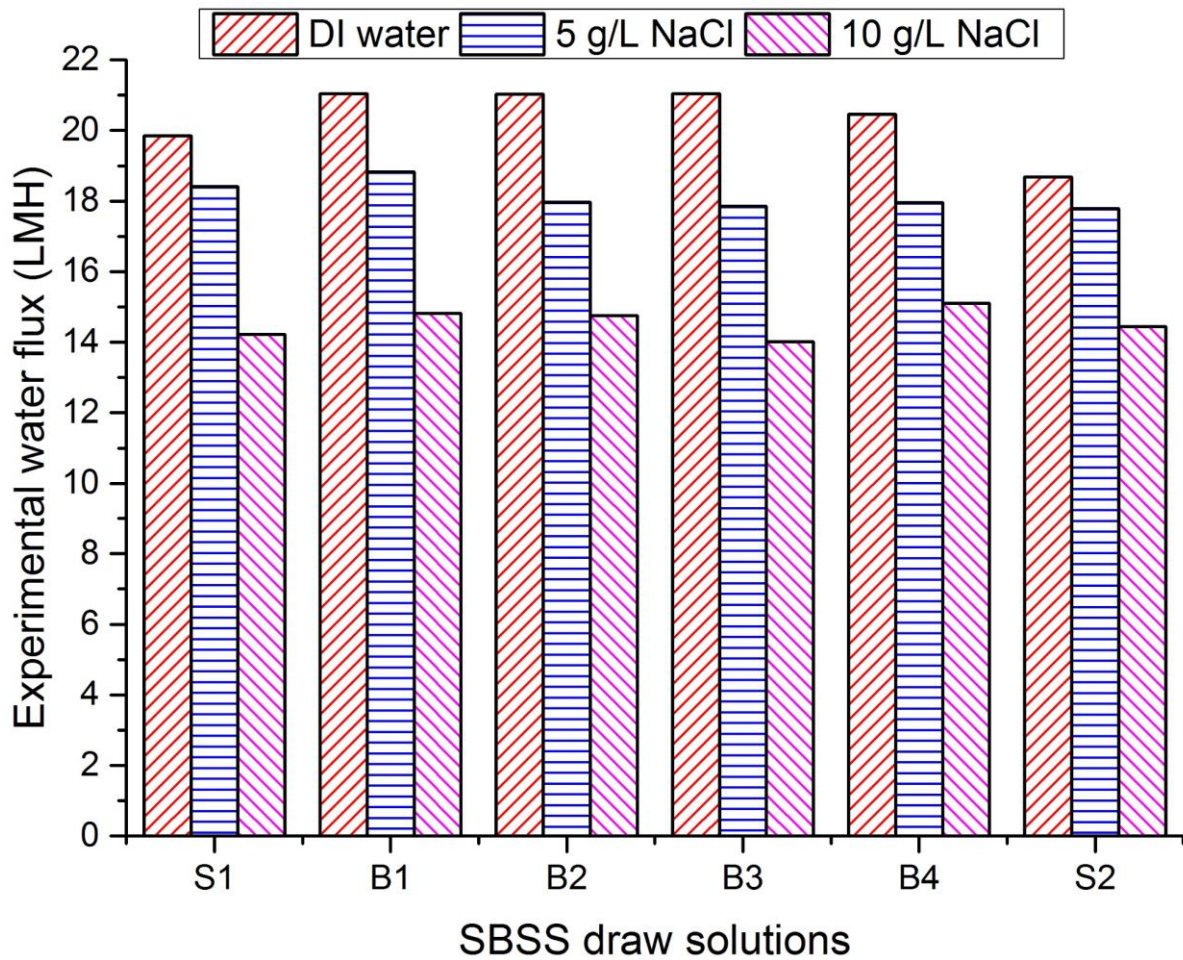
297 Figure 4 Specific reverse solute flux of individual solute (ion) permeating from SBSS draw  
 298 solutions into feed solution (DI water) using CTA FO membrane and TFC FO membrane.

299

300 At the end of experiments, feed solutions samples were collected and analysed for  $NH_4^+$  ,  
 301  $SO_4^{2-}$  and  $SO_3^{2-}$  . Analyzing concentration of ions in FS was to identify the amount of individual  
 302 ion lost into FS for comparative purpose only. Figure 4 shows the individual SRSF of three  
 303 major ions permeated into FS. Generally, among all SBSS DSs, concentrations of individual  
 304 ions permeated from SBSS DS into FS, as CTA membrane was used, were twice as high as that  
 305 when TFC membrane was used. The results indicating the increase in ammonium SRSF were  
 306 the primary cause of increase in total SRSF of SBSS draw solutions. For instance, for S1 in both  
 307 cases (using TFC and CTA membranes), sulfate SRSF was slightly higher than that of  
 308 ammonium SRSF while sulfite SRSF was the lowest one. However, for DSs B1, B2, B3 and B4

309 containing SIOA and SOA, ammonium SRSF sharply escalated by 4 to 8 times and 3 to 6 times  
310 as CTA membrane and TFC membrane were used respectively. While sulfite SRSF remained  
311 stable with both membranes, sulfate SRSF slightly increased using CTA membrane and  
312 gradually dropped using TFC membrane. The dramatic rise of ammonium SRSF can be  
313 explained by the combined effects of (i) charge effect (attractive force) between a positively  
314 charged ammonium ion and the negatively charged TFC membrane surface thereby  
315 enhancing RSF; (ii) smaller effective diameter of hydrated ammonium  $NH_4^+$  (0.301 nm)  
316 compared to that of sulfate  $SO_4^{2-}$  (0.393 nm) and sulfite  $SO_3^{2-}$  (0.380 nm) [39]; and (iii) the  
317 increase of ammonium ion diffusivity.~~the increase in diffusivity of this solute and its smaller~~  
318 ~~effective diameter of hydrated ammonium  $NH_4^+$  (0.301 nm) compared to that of sulfate  $SO_4^{2-}$~~   
319 ~~(0.393 nm) and sulfite  $SO_3^{2-}$  (0.380 nm) [39].~~ This makes ammonium ions ( $NH_4^+$ ) easy to pass  
320 through the membrane pores [11]. These findings were vitally important for FDFO  
321 desalination process in search for resolutions to hinder the increase of SRSF when using SBSS  
322 as draw solutions for FDFO process.

323 The experimental results using different SBSS DS indicate that B1 and S1 are the most suitable  
324 DS for FDFO process for both the TFC and CTA FO membranes. This shows that SBSS DS  
325 containing lower concentrations of SIOA is more preferable for FDFO process and this is only  
326 possible by ensuring complete oxidation of SIOA to SOA prior to its use as DS in the FDFO  
327 desalination process. Pre-oxidation of SIOA could also be essential to prevent the plants from  
328 sulfite toxicity. The sulfite ions such as  $SO_3^{2-}$  and  $HSO_3^-$  are strong nucleophile, which can  
329 detrimentally affect plant health. The symptoms include leaf chlorosis, necrosis and long-term  
330 yield reduction [40-42]. Hence, less sulfite in SBSS DS will reduce the risk for plant health and  
331 productivity.



333

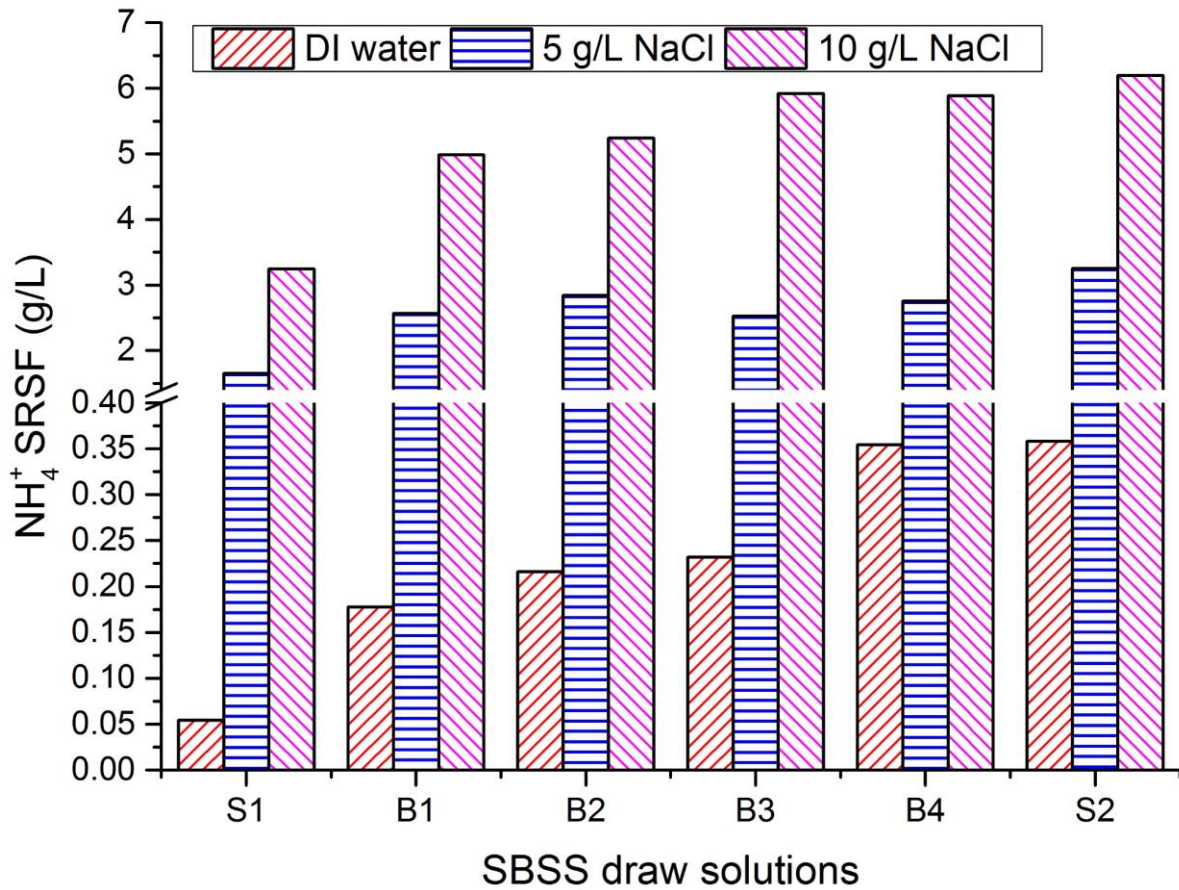
334 Figure 5. Experimental water flux (LMH) (SBSS draw solutions and model feed solutions with  
 335 DI water and different NaCl concentrations, experiment at duration of 8 hours).

336

337 The performances of SBSS DS for FDFO desalination process were also assessed with two  
 338 model feed solutions containing 5 and 10 g/L of NaCl to represent two types of brackish water  
 339 with different levels of salinity and their results are presented in Figure 5. As expected, the  
 340 water fluxes of the FDFO process using TFC FO membrane decrease drastically when higher  
 341 salinity FS is used. For instance, the water flux for B1 DS dropped from 18.8 LMH for 5 g/L  
 342 NaCl FS to 14.8 LMH for 10 g/L NaCl FS. The decrease in the water flux at higher salinity is  
 343 attributed to decrease in the osmotic driving force due to lower net bulk osmotic pressure

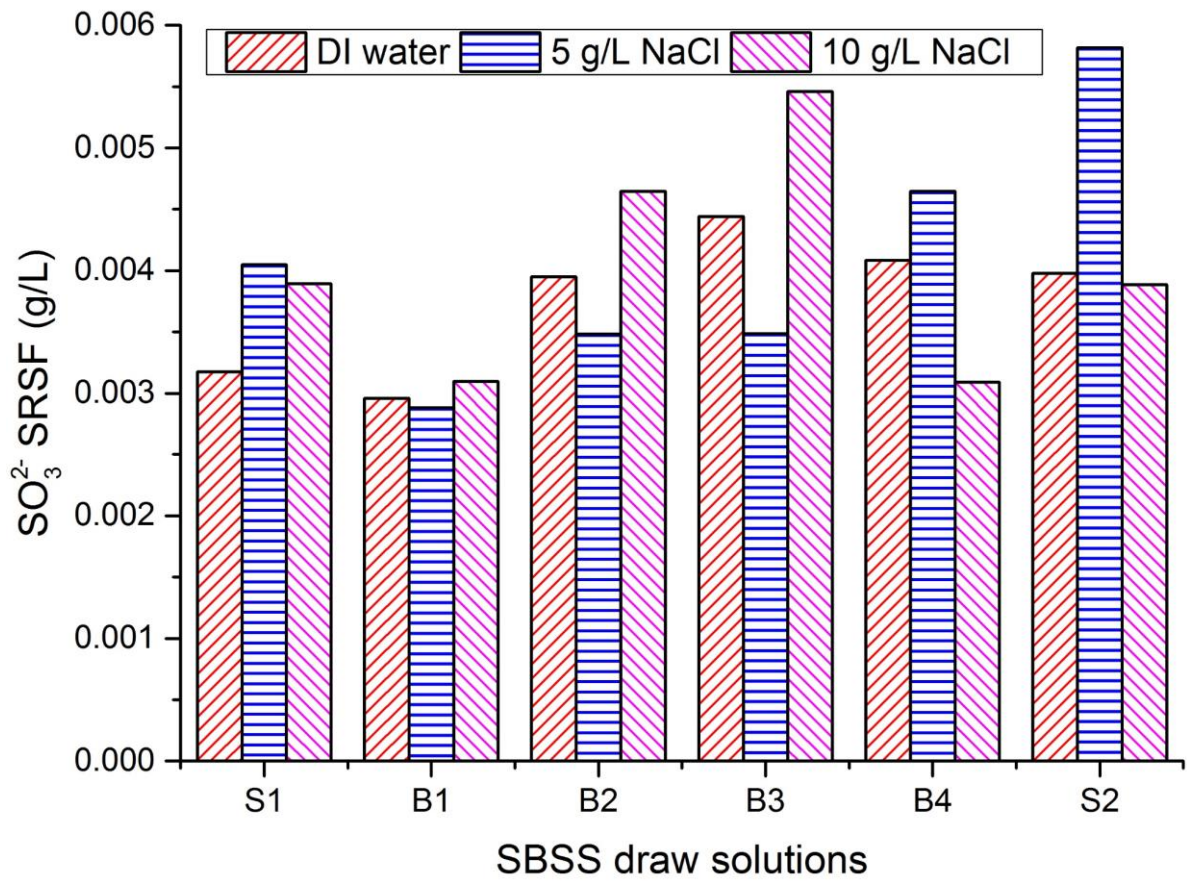
344 differential between DS and FS [30, 32]. Among the six SBSS DSs tested in this study, B1  
345 showed the highest experimental water fluxes. This finding complements the earlier  
346 observation that B1 slightly performed better compared to that of other SBSS draw solutions.

347 **3.2.1 Specific reverse water flux (SRSF)**



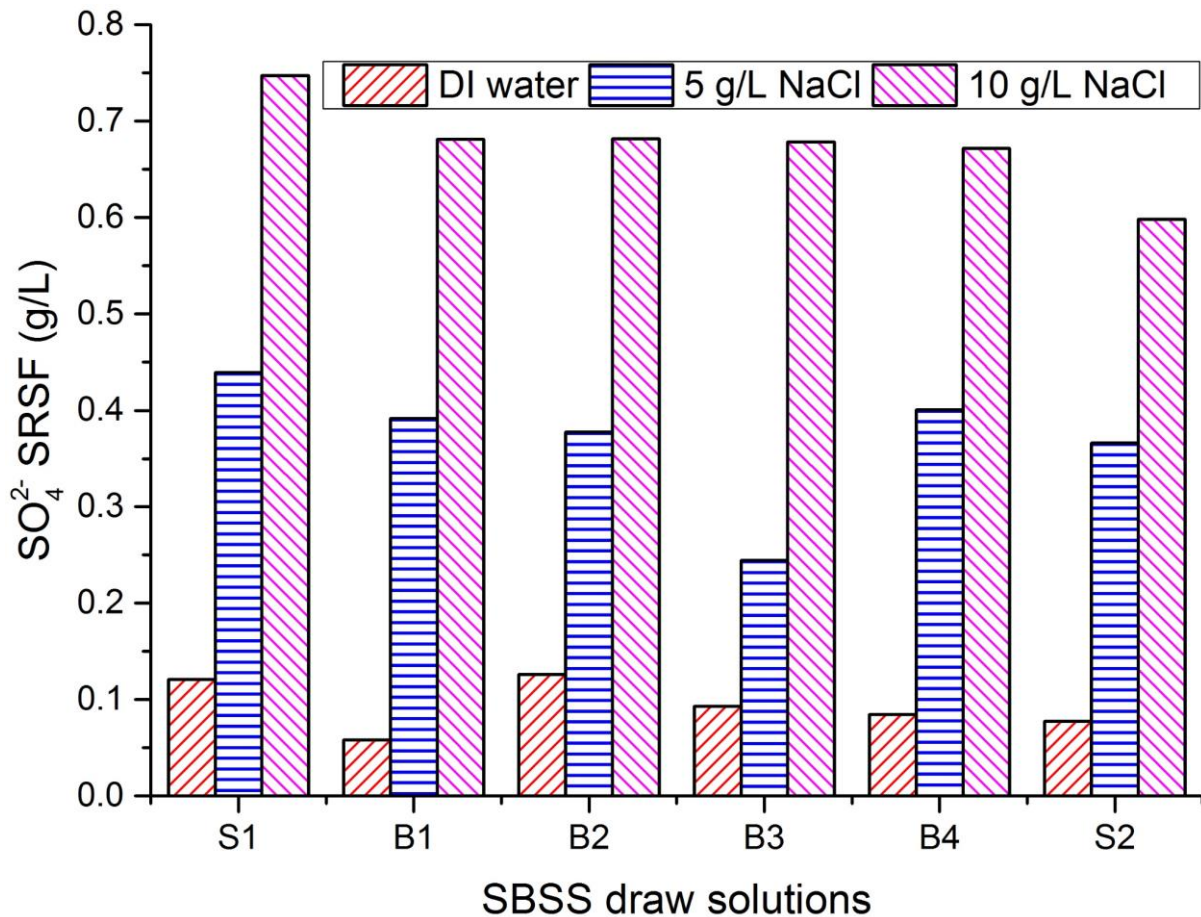
348

349 Figure 6. Specific reverse solute flux of ammonium ion ( $\text{NH}_4^+$ ) (SBSS draw solutions and model  
350 feed solutions with different NaCl concentrations, experiment duration of 8 hours).



351

352 Figure 7. Specific reverse solute flux of sulfite ion ( $\text{SO}_3^{2-}$ ) (SBSS draw solutions and model feed  
 353 solutions with different NaCl concentrations, experiment at duration of 8 hours).



354

355 Figure 8. Specific reverse solute flux of sulfate ion ( $\text{SO}_4^{2-}$ ) (SBSS draw solutions and model feed  
 356 solutions with different NaCl concentrations, experiment at duration of 8 hours).

357

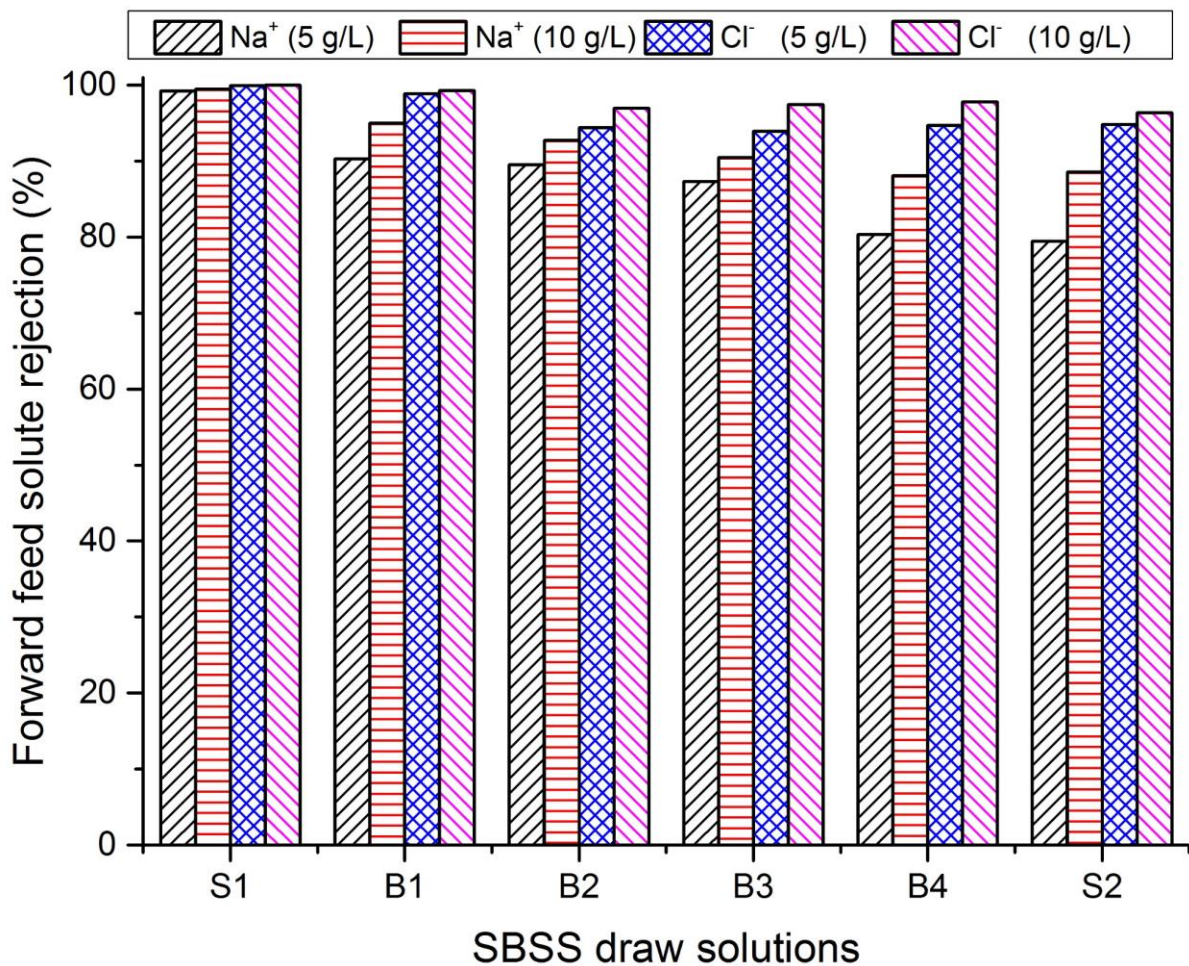
358 When model saline water having TDS equivalent to 10 g/L NaCl was used as FSs, FDFO  
 359 desalination process generally produced the highest SRSF values ranging from 4 – 6 g/L. Lower  
 360 SRSF values varying from 2 to 3.6 g/L were generated by using model saline water having TDS  
 361 equivalent to 5 g/L NaCl as FSs. These SRSF values in these cases were significantly higher than  
 362 that using DI water at approximately 0.2 to 0.3 g/L. The higher SRSF values of FDFO  
 363 desalination process using 10 g/L NaCl FS can be attributed to the dramatic increase of reverse  
 364 solute flux in association with the sharp decrease of experimental water flux. This finding  
 365 proved that for FDFO desalination process, the most suitable FS is brackish water having low  
 366 TDS equivalent to 5 g/L NaCl.



367 Figures 6-8 showed the specific reverse solute flux of individual cations and anions permeated  
368 from the DS to the FS. These results were calculated based on the analysis of ion  
369 concentration in the FS sample collected at the end of experiments and equations (1-3). For  
370 ammonium  $NH_4^+$  SRSF, this cation showed the highest SRSF value in three cases using three  
371 different types of FS compared to the two anions. The  $NH_4^+$  SRSF sharply increased when the  
372 feed solution concentration changed from DI water to 5 g/L and 10 g/L NaCl. It was at about  
373 1.65 to 3.25 g/L with 5 g/L NaCl FS before reaching to 3.24 to 6.20 g/L with 10 g/L NaCl FS.  
374 Similarly, the  $SO_4^{2-}$  SRSF followed the identical trend, however, its values were significantly  
375 lower (about four to five times lower) in comparison to that of  $NH_4^+$  SRSF. Interestingly, there  
376 were only slight changes in the rates of sulfite  $SO_3^{2-}$  diffusion using the first two model feed  
377 solutions, and it then dramatically increased when using 10 g/L NaCl FS. The phenomenon of  
378 dramatic increase in cation diffusion and mild enhancement in anion diffusion with TFC  
379 polyamide membranes under similar conditions used in this study, was also reported in some  
380 previous studies [37, 43, 44]. It can be attributed to the presence of  $Na^+$  in FS, which might  
381 exponentially enhance the reverse transport of  $NH_4^+$  for TFC polyamide membranes. Another  
382 possible explanation for the enhancement of bidirectional diffusion of these two cations is  
383 the existence of carboxyl group in the functional groups of TFC membrane [37, 45]. This  
384 functional group is influenced by pH of the two solutions, and thus TFC membranes become  
385 more negatively charged. The membrane active layer then functions as a cation exchanger  
386 [46, 47]. Lu et al. [43] stated that the main mechanism responsible for the enhanced  
387 bidirectional diffusion of cations in TFC membranes is Donnan dialysis. Due to its high  
388 electrostatic attraction to the negatively charged polyamide surface and its high  
389 concentration of  $NH_4^+$  in DS side, and its small effective hydrated diameter,  $NH_4^+$  readily  
390 diffuses through the TFC membrane from DS to FS. The initial diffusion of  $NH_4^+$  generates the

391 positive and negative charge potentials in the FS and DS. To maintain the electro-neutrality,  
 392 two anions  $SO_3^{2-}$  and  $SO_4^{2-}$  will automatically diffuse from draw side to feed side, or cation  
 393  $Na^+$  in the feed side will pass through the TFC membrane to the draw side. While the  
 394 transport of two anions was hindered by electrostatic generated by the negatively charged  
 395 surface, cation in FS namely  $Na^+$  readily adsorbs onto the negatively charged membrane  
 396 surface and diffuses through the polyamide layer, which explains the enhanced bidirectional  
 397 diffusion of cations for the TFC membrane.

398 **3.3 Forward rejection of feed solute ions**



399

400 Figure 9. Rejection of feed solute ions from FS to DS by different SBSS draw solutions and feed  
 401 solutions

402 The highest feed solute rejection rate (forward rejection) was obtained using S1 exceeding  
403 99%. The rejection of cation  $\text{Na}^+$ , however, dramatically decreased compared to  $\text{Cl}^-$  rejection  
404 for SBSS DS containing higher SIOA concentrations as observed with all three FS. Besides,  $\text{Na}^+$   
405 rejection was also consistently lower compared to  $\text{Cl}^-$  rejection under all the conditions tested  
406 in this study. This low rejection of  $\text{Na}^+$  is likely to be attributed to the bidirectional diffusion  
407 of cations through the TFC FO membrane since the cations on both sides of the membranes  
408 ( $\text{Na}^+$  and  $\text{NH}_4^+$ ) are much smaller compared to the sizes of the anions ( $\text{Cl}^-$  and  $\text{SO}_4^{2-}$  or  $\text{SO}_3^{2-}$ )  
409 and hence can more readily diffuse compared to anions.

410 Among these two FSs, TFC membrane indicated the lowest rejection of forward feed solute  
411 using 5 g/L NaCl FS. As FS concentration increased from 5 g/L to 10 g/L NaCl, the rejection of  
412 forward feed solute increased although the feed solute forwardly diffused from FS to DS  
413 increased. This is due to the significantly faster increase in concentration of initial  
414 concentration of  $\text{Na}^+$  and  $\text{Cl}^-$  in FS compared to the rise of forward solute flux in DS. Therefore,  
415 although 10 g/L NaCl FS achieved the highest rejection, the forward solute flux was still  
416 highest and this is undesirable condition for FDFO process as forward solute flux might require  
417 removal of feed solute before using diluted DS for fertigation. This definitely increases the  
418 cost of FDFO desalination process, which makes this technology less attractive.

#### 419 **4 Conclusions**

420 In this current work, feasibility of using sulfur-based seed solution (SBSS), a by-product from  
421 photoelectrochemical (PEC) water splitting process, was thoroughly investigated by  
422 evaluating performance of fertilizer drawn forward osmosis (FDFO) desalination process. Six  
423 SBSS draw solutions with different composition ratios of ammonium sulfate (SOA) and  
424 ammonium sulfite (SIOA) were investigated in FDFO desalination of three types of feed

425 solution (model brackish groundwater and seawater) in the feed side. The primary findings  
426 from this study are summarized herein below:

- 427 • SBSS draw solution was successfully tested and can be used as fertilizer draw solution  
428 in FDFO desalination process with better performance (i.e. water flux, PR, SRSF) when  
429 TFC membrane was utilized compared to CTA membrane during the investigation.
- 430 • Among six SBSS draw solutions examined in this study, B1 containing least ammonium  
431 sulfite (SIOA –  $(\text{NH}_4)_2\text{SO}_3$ ), produced the highest water flux when using TFC membrane  
432 (21 LMH) in comparison with using CTA membrane (11 LMH) under the test conditions  
433 with deionized water as feed solution. FDFO process also presented the least value of  
434 specific reverse solute flux (SRSF) when using B1 and TFC membrane.
- 435 • SBSS draw solutions tested showed the most suitable for FDFO desalination process  
436 of brackish water having the total dissolved solids equivalent to 5 g/L NaCl. Using  
437 model brackish ground water and TFC membrane, B1 exhibited the highest  
438 experimental water flux of approximately 19 LMH.
- 439 • Results indicated that the less SIOA that SBSS draw solution contains, the better  
440 performance of FDFO desalination process was (higher water flux and lower SRSF).  
441 The performance was influenced by the pH of SBSS draw solution in which lower pH  
442 of SBSS produced higher water flux and lower SRSF. Therefore, less concentration of  
443 SIOA in SBSS is desirable because of several reasons such as (i) higher osmotic  
444 pressure; (ii) higher water flux and lower SRSF; (iii) less sulfite toxicity for plant.
- 445 • Oxidation rate of ammonium sulfite in SBSS might play an important role since it favors  
446 the FDFO desalination process. However, according to our experimental results,  
447 oxidation rate of sulfite under the condition of FDFO desalination process was almost  
448 at zero. It is also recommended for further investigation of this oxidation rate.

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455

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