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## A Novel Multi-Charged Draw Solute That Removes Organic Arsenicals from Water in a Hybrid Membrane Process

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1 A Novel Multi-Charged Draw Solute That Removes  
2 Organic Arsenicals from Water in a Hybrid  
3 Membrane Process

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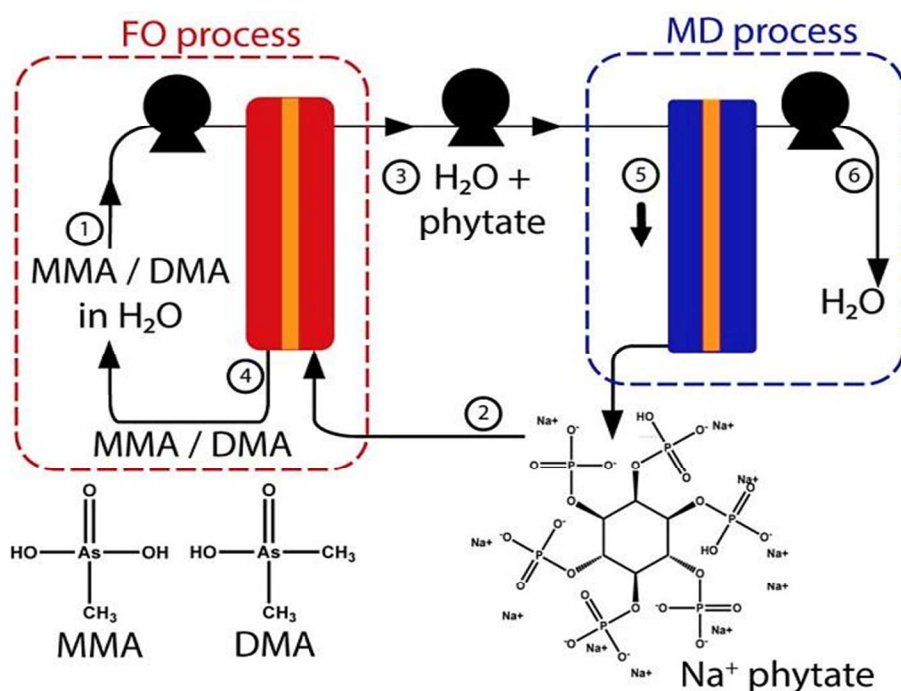
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10 **ABSTRACT:** The potential of forward osmosis for water treatment can only be maximized  
11 with suitable draw solutes. Here a three-dimensional, multi-charge draw solute of decasodium  
12 phytate (Na<sub>10</sub>-phytate) is designed and synthesized for removing organic arsenicals from water  
13 using a hybrid forward osmosis (FO) – membrane distillation (MD) process. Efficient water  
14 recovery is achieved using Na<sub>10</sub>-phytate as a draw solute with a water flux of 20.0 LMH and  
15 negligible reverse solute diffusion when 1000 ppm organic arsenicals as the feed and operated  
16 under ambient conditions with FO mode. At 50 °C, the novel draw solute increases water flux by  
17 more than 30 % with water fluxes higher than 26.0 LMH on the FO side, drastically enhancing

18 water recovery efficiency. By combining the FO and MD processes into a single hybrid process,  
 19 a 100% recovery of Na<sub>10</sub>-phytate draw solute was achieved. Crucially, organic arsenicals or  
 20 Na<sub>10</sub>-phytate draw solutes are both rejected 100% and not detected in the permeate of the hybrid  
 21 process. The complete rejection of both organic arsenicals and draw solutes using hybrid  
 22 membrane processes is unprecedented; creating a new application for membrane separations.

### 23 ■ TOC Art



24

25

### 26 ■ INTRODUCTION

27 Arsenic contamination of water resources arise from their natural geological presence in deep  
 28 underground water sources or from anthropogenic activities such as mining, farming, and wood  
 29 preservation.<sup>1-3</sup> Arsenic can exist as toxic (inorganic or organic) and nontoxic (organic content in  
 30 seafood) forms.<sup>1,3</sup> The toxicity of arsenic depends on valence state, solubility, physical state and

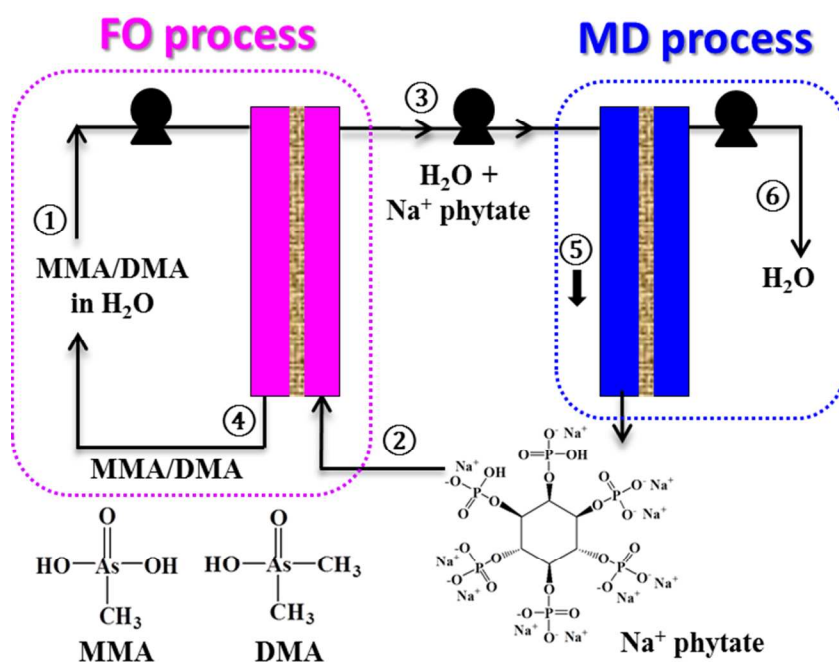
31 purity, rates of absorption and elimination. In general, the toxicity of arsenicals is as follows:  
32 Inorganic trivalent > organic trivalent > inorganic pentavalent > organic pentavalent > elemental  
33 arsenic.<sup>4-6</sup> The toxicity of various arsenic forms guides the design of current arsenic removal  
34 technologies. Traditionally, inorganic arsenic compounds were perceived to be more toxic and  
35 potent than organic arsenicals.<sup>4,7</sup> Hence, conventional technologies such as adsorption, ion  
36 exchange, coagulation, and membrane separations (nanofiltration, reverse osmosis, and  
37 electro dialysis) were investigated for removing inorganic arsenicals.<sup>6-8</sup>

38 Despite the extensive applications of these technologies for arsenical removal, the following  
39 problems are widely present. Large volumes of arsenic-rich sludge and waste can be generated  
40 using adsorption and coagulation,<sup>2,9-11</sup> while membrane separation technologies consume large  
41 amounts of energy.<sup>6,12-14</sup> The removal of organic arsenic has become increasingly important as  
42 methyl derivatives of arsenic that are omnipresent in agriculture (monomethylarsenic – MMA,  
43 dimethylarsenic – DMA) present a carcinogenic risk.<sup>4</sup> Moreover, inorganic arsenic compounds  
44 can convert into methylated arsenicals under appropriate conditions.<sup>7</sup> Clearly, there is a need to  
45 develop a green and cost-effective bespoke technology for removing organic arsenicals.

46 Here we propose to use a hybrid forward osmosis (FO) – membrane distillation (MD) process  
47 to remove organic arsenicals (Figure 1). FO-MD is an economical and sustainable technology to  
48 treat wastewater,<sup>15</sup> concentrate protein solutions,<sup>16</sup> and desalination.<sup>17</sup> This technology separates  
49 water from dissolved solutes (contaminants or proteins) using the operating principle  
50 underpinning FO processes while recovering the draw solute using MD. An osmotic pressure  
51 difference is first generated by a concentration gradient using a “draw” solution with higher  
52 concentration of dissolved solutes in relation to the feed solution. Water from the feed solution  
53 permeates across the membrane, while the contaminants are retained in the FO feed. The FO

54 permeate now contains a dilute mixture of water and draw solute that requires MD to recover the  
 55 draw solute while producing high purity water. Clearly, the crux of this hybrid process is the  
 56 draw solutes.<sup>18</sup> Suitable draw solutes can enhance FO performance, i.e. achieving high water  
 57 recovery whilst avoiding secondary contamination at lower costs, and recovered. Conventional  
 58 draw solutes such as NaCl,<sup>19</sup> MgCl<sub>2</sub><sup>20</sup> and glucose saccharide<sup>20</sup> have been deployed for removing  
 59 inorganic arsenics, but to minimal effect. This is attributed to either low water permeation flux,  
 60 or/and severe reverse solute diffusion.

61



62

63 **Figure 1.** Using Na<sub>10</sub>-phytate draw solute to treat water that contains MMA and DMA via a FO process.

64 Subsequently, the draw solute is dehydrated and regenerated using an in-line MD process.

65 Excellent draw solutes that optimize FO processes are typically pH-neutral, easily ionized  
 66 compounds that generate large osmotic pressures.<sup>21,22</sup> These compounds produce a neutral  
 67 solution that does not degrade the membrane during FO, whilst providing a large driving force  
 68 for water transport. Draw solutes with a suitable spatial configuration and high ionization degree

69 are critical for producing a high water recovery and minimizing reverse solute diffusion across  
70 the membrane in FO.<sup>22</sup> Guided by these requirements, we design and synthesize a novel phytate  
71 ( $\text{Na}_{10}$ -phytate) and demonstrate the advantages of this new compound as a draw solute to remove  
72 organic arsenicals from water. First, water fluxes of up to 20 LMH (FO mode) are achieved at  
73 room temperature when  $\text{Na}_{10}$ -phytate is deployed in single FO processes. Second, we observed  
74 negligible reverse solute diffusion during MMA or DMA removal even at 50 °C. Finally, we  
75 show that MMA or DMA can be completely removed from water while the  $\text{Na}_{10}$ -phytate draw  
76 solutes are fully recovered and regenerated.

## 77 ■ MATERIALS AND METHODS

78 **Syntheses of  $\text{Na}_{10}$ -Phytate.**  $\text{Na}_{10}$ -phytate was synthesized through the neutralization reaction  
79 between phytic acid and NaOH. The experimental details were given in the supporting  
80 information (SI).

81 **Determination of the Sodium ion Numbers in  $\text{Na}_{10}$ -Phytate.** The number of sodium ions in  
82 the synthesized sodium phytate was determined via acid-base titration. The detailed information  
83 was provided in the SI.

84 **Characterization of  $\text{Na}_{10}$ -Phytate.** Elemental analyses, the size distribution of  $\text{Na}_{10}$ -phytate in  
85 its aqueous solution, and thermogravimetric analysis (TGA) measurement were used to  
86 determine the chemical composition of  $\text{Na}_{10}$ -phytate and its state in solution prior to the FO  
87 applications. The experimental details were included in the SI.

88 **Determination of the Physicochemical Properties of the  $\text{Na}_{10}$ -Phytate Solution.** The  
89 physicochemical properties of the  $\text{Na}_{10}$ -phytate solution were determined by analyzing their  
90 relative viscosity and osmotic pressures. Details were provided in the SI.

91 **FO Processes.** The FO experiments were carried out through a bench-scale FO set-up as  
92 established elsewhere.<sup>23</sup> Commercial HTI flat sheet membranes and home-made thin-film  
93 composite (TFC) FO membranes fabricated on polyethersulfone (PES) hollow fibers (TFC-  
94 PES)<sup>24</sup> were both used in the FO experiments. The detailed experimental conditions were  
95 provided in the SI.

96 **Preparation and Analyses of MMAs and DMAs Solutions.** The MMAs and DMAs  
97 solutions were prepared from  $\text{CH}_4\text{AsNaO}_3$  and  $(\text{CH}_3)_2\text{AsNaO}_2$ , respectively. The pH values of  
98 these solutions were maintained using HCl and NaOH. The experimental details of the  
99 MMAs/DMAs solution preparation and analyses were included in the SI.

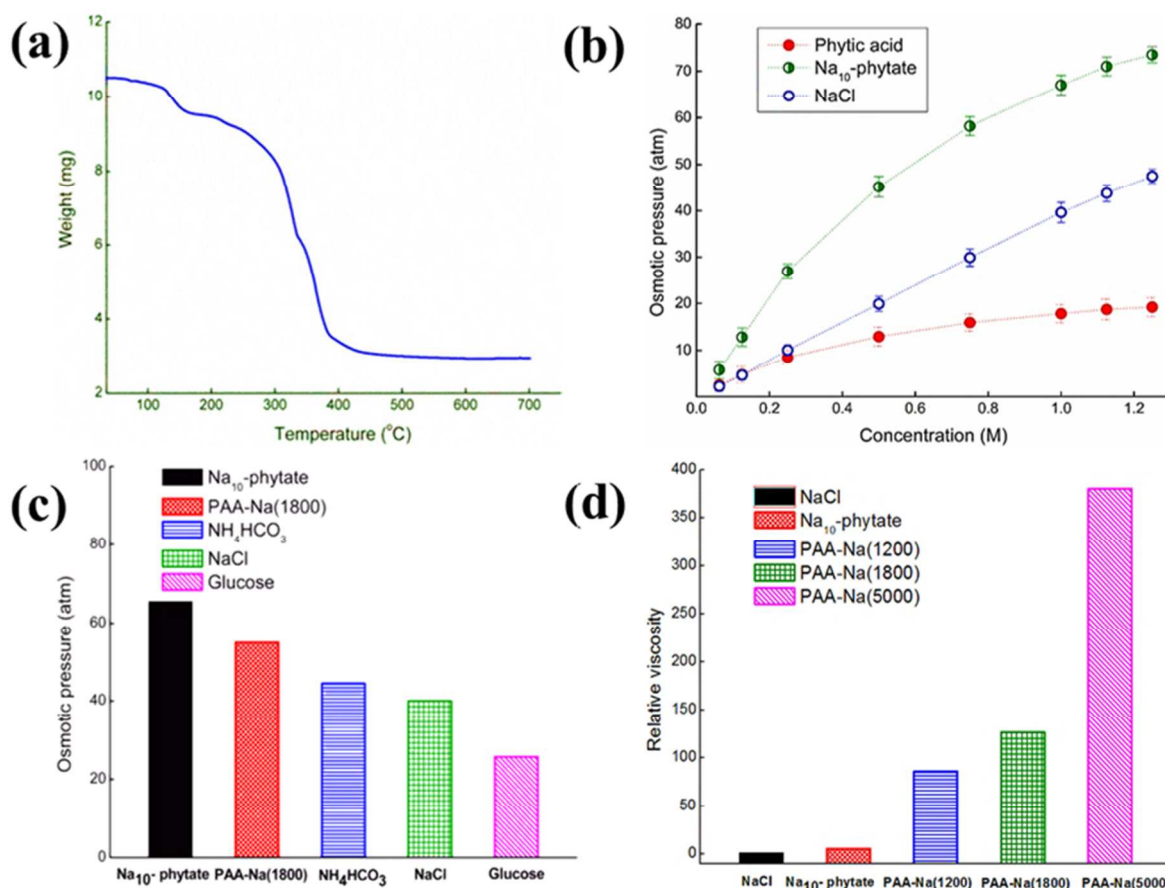
100 **Regeneration of  $\text{Na}_{10}$ -Phytate Solute.** An MD set-up with home-made PVDF hollow fiber  
101 membranes<sup>25</sup> was employed to concentrate the diluted  $\text{Na}_{10}$ -phytate solution after FO. The  
102 experimental details were disclosed in the SI.

## 103 ■ RESULTS AND DISCUSSION

104 **Synthesis and Characterization of  $\text{Na}_{10}$ -Phytate.** Phytic acid, a hexaphosphate polyacid, was  
105 neutralized with a known volume and molar concentration of sodium hydroxide (NaOH) to  
106 produce a three-dimensional, multi-charge decasodium phytate ( $\text{Na}_{10}$ -phytate) neutral draw  
107 solute. The leftover NaOH solution was titrated with hydrochloric acid (HCl); revealing a 1:10  
108 ratio of phytic acid to sodium hydroxide i.e. there are 10  $\text{Na}^+$  ions in the phytate.  
109 Thermogravimetric analysis (TGA) was used to confirm the elemental composition of the  
110 phytate developed here in this work. Thermal decomposition of  $\text{Na}_{10}$ -phytate occurred in two  
111 stages. The first stage corresponds to a release of water molecules between 122 – 155 °C;  
112 accounting for a weight loss of 9.5 wt. % (Table S1). The second stage at 205 – 398 °C correlates  
113 to the decomposition of 63.8 wt. % of dehydrated organic phosphate salt (Figure 2a). The residue



114 (26.7 wt. %) comprises mainly sodium oxides. Weight losses associated with these two stages  
 115 are in excellent comparison with theoretical calculations carrying crystal water molecules.



116  
 117 **Figure 2.** (a) TGA analysis of  $\text{Na}_{10}$ -phytate demonstrating its thermal stability up to 205 °C. (b)  
 118 The osmotic pressures of the precursor compound – phytic acid, conventional draw solute –  
 119 NaCl, and the novel draw solute developed in this work –  $\text{Na}_{10}$ -phytate. (c) An osmotic pressure  
 120 comparison of  $\text{Na}_{10}$ -phytate with traditional draw solutes. (d) A relative viscosity comparison of  
 121  $\text{Na}_{10}$ -phytate with other draw solutes.

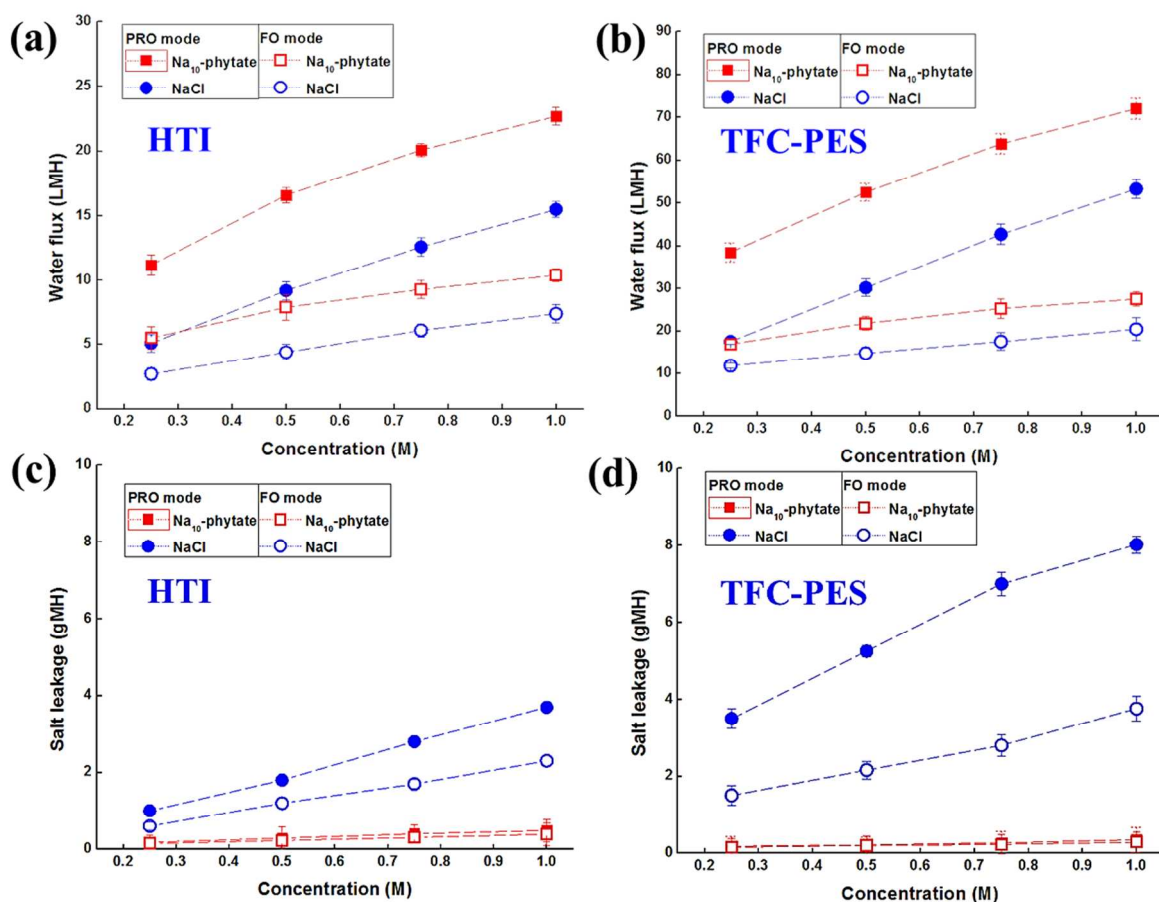
122 Important material characteristics that govern applications as FO draw solutes include osmotic  
 123 pressure and relative viscosity. We observe that both osmotic pressure and relative viscosity of  
 124  $\text{Na}_{10}$ -phytate increase non-linearly with higher concentrations (Fig. 2b, Fig. S1). This can be  
 125 ascribed to the relatively large configuration and chemical composition of  $\text{Na}_{10}$ -phytate. The

126 hydrophilic functional groups of Na<sub>10</sub>-phytate can ionize into multi-charge anions and multiple  
127 cations in aqueous solutions. Predicted by the Van't Hoff equation,<sup>26</sup> the dissociation of Na<sub>10</sub>-  
128 phytate into multiple ionic species increases the number of solute particles in the aqueous  
129 solution; generating an osmotic pressure (66 atm) which is 65 % larger than that of NaCl at 1.0  
130 M, the conventional draw solute in FO (Figure 2b). At low concentrations, salts dissociate  
131 completely into multiple ionic species; generating large increments in osmotic pressures.<sup>27</sup> This  
132 is impeded at higher concentrations. However, the osmotic pressure generated by 1.0 M of Na<sub>10</sub>-  
133 phytate is significantly higher than those of synthetic draw solutes such as magnetic  
134 nanoparticles,<sup>28</sup> polyelectrolytes,<sup>29</sup> hydrogels<sup>30</sup> and many others<sup>22,31</sup> (Figure 2c). Meanwhile the  
135 relative viscosity ( $\eta_r$ ) of Na<sub>10</sub>-phytate is at least 60 % lower than polyelectrolytes<sup>29</sup> (Figure 2d),  
136 and is comparable to NaCl. Compounds with a reduced relative viscosity are preferred as draw  
137 solutes for FO processes as less internal concentration polarization will be caused and water  
138 molecules can easily diffuse across the membrane towards the permeate side. The good thermal  
139 stability, high osmotic pressure, and low relative viscosity of Na<sub>10</sub>-phytate are ideal for FO.

140 **Na<sub>10</sub>-phytate as a FO Draw Solute.** Initial screening tests (Figure 3) indicated that FO is  
141 optimized with a home-made thin film composite (TFC) – polyethersulfone (PES) hollow fiber  
142 membrane.<sup>24</sup> Regardless of membrane orientation (the active layer facing feed solution i.e. FO  
143 mode or the active layer facing draw solution containing 0.5 M of Na<sub>10</sub>-phytate – pressure  
144 retarded osmosis (PRO) mode), the water flux of a TFC-PES membrane is 3 times higher than  
145 that of a commercial flat sheet membrane from HTI. Coupled with an insignificant salt leakage  
146 rate, the TFC-PES membrane in FO mode is ideal for FO water treatment. The drastically higher  
147 water flux is ascribed to membrane structural configuration where the thin TFC selective layer  
148 supported on a porous PES substrate has lower water transfer resistance relative to the dense and

149 thick HTI membrane.<sup>24</sup> Meanwhile the spatial structure and chemical composition of Na<sub>10</sub>-  
 150 phytate contribute to a negligible reverse solute diffusion. In Na<sub>10</sub>-phytate, the evenly-distributed  
 151 phosphates around an aromatic carbon ring develop a three-dimensional structure that form  
 152 hydrogen-bond with water molecules in the aqueous solution (Figure S2a). This supramolecular  
 153 structure inhibits reverse diffusion; minimizing leakage rates. The size distribution of the  
 154 supramolecular network falls in a range much larger than that of an FO membrane pore size  
 155 which accounts for the negligible leakage of Na<sub>10</sub>-phytate (Figure S2b).

156



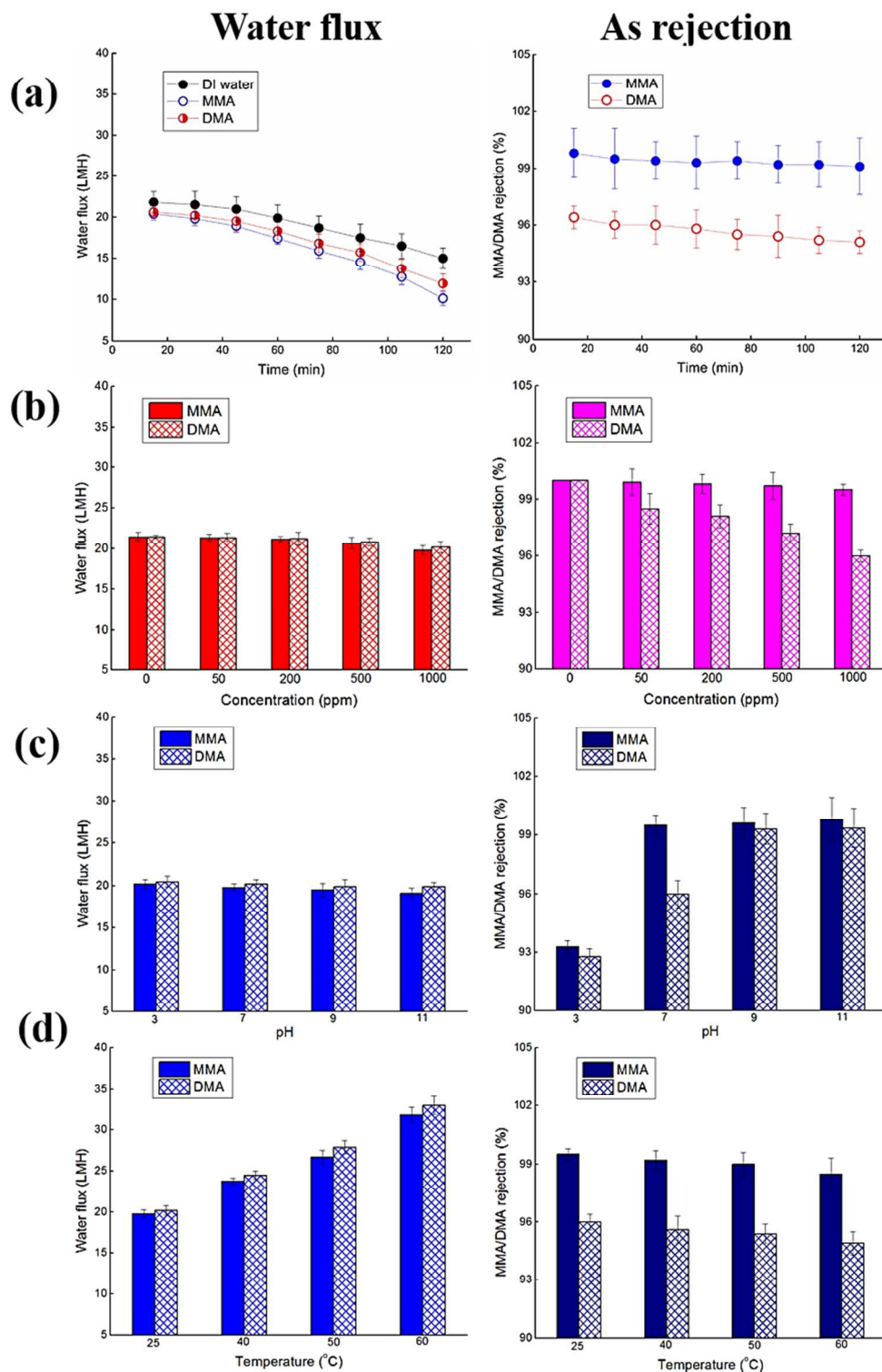
157

158 **Figure 3.** Effects of draw solute concentration, membrane and membrane orientation on FO performance:

159 (a) water flux of HTI membrane; (b) water flux of TFC-PES membrane; (c) salt leakage of HTI

160 membrane; (d) salt leakage of TFC-PES membrane. DI water as the feed solution.

161 We investigated the impact of Na<sub>10</sub>-phytate as a draw solute to remove organic arsenicals in a  
162 FO process using TFC-PES hollow fiber membranes at FO operation times between 20 to 120  
163 mins, MMA or DMA concentrations ranging from 0 – 1000 ppm, pH between 3 to 11, and  
164 temperatures from 25 to 60 °C. These parameters are key for creating an osmotic pressure  
165 differential across the membrane to drive FO water treatment. Longer operation times (20 to 120  
166 min) reduced water flux by 20 % with the DI water feed, possibly due to water transfer  
167 concentration polarization and/or membrane fouling (Figure 4a). Water flux is reduced by 35 and  
168 45 % with 1000 ppm of DMA or MMA, respectively. Organic arsenicals in the feed solution  
169 enhance feed osmotic pressure; reducing the net driving force across the membrane, hence  
170 further decreasing water flux. The higher concentration of anions in a MMA solution (relative to  
171 DMA solution) can dissociate into more ionic solute particles;<sup>9</sup> generating a slightly higher  
172 osmotic pressure. Thus, a lower water flux was observed with MMA present in the feed solution.  
173 The high anion concentration in MMA solutions creates a stronger charge repulsion with the  
174 surface of the electronegative TFC-PES membrane; rejecting more than 99.5 % of MMA.



175

176 **Figure 4.** FO performances (water flux and organic As rejection) for removing MMA or DMA from

177 water using TFC-PES hollow fiber membranes at various operating conditions: (a) 20 – 120 mins of

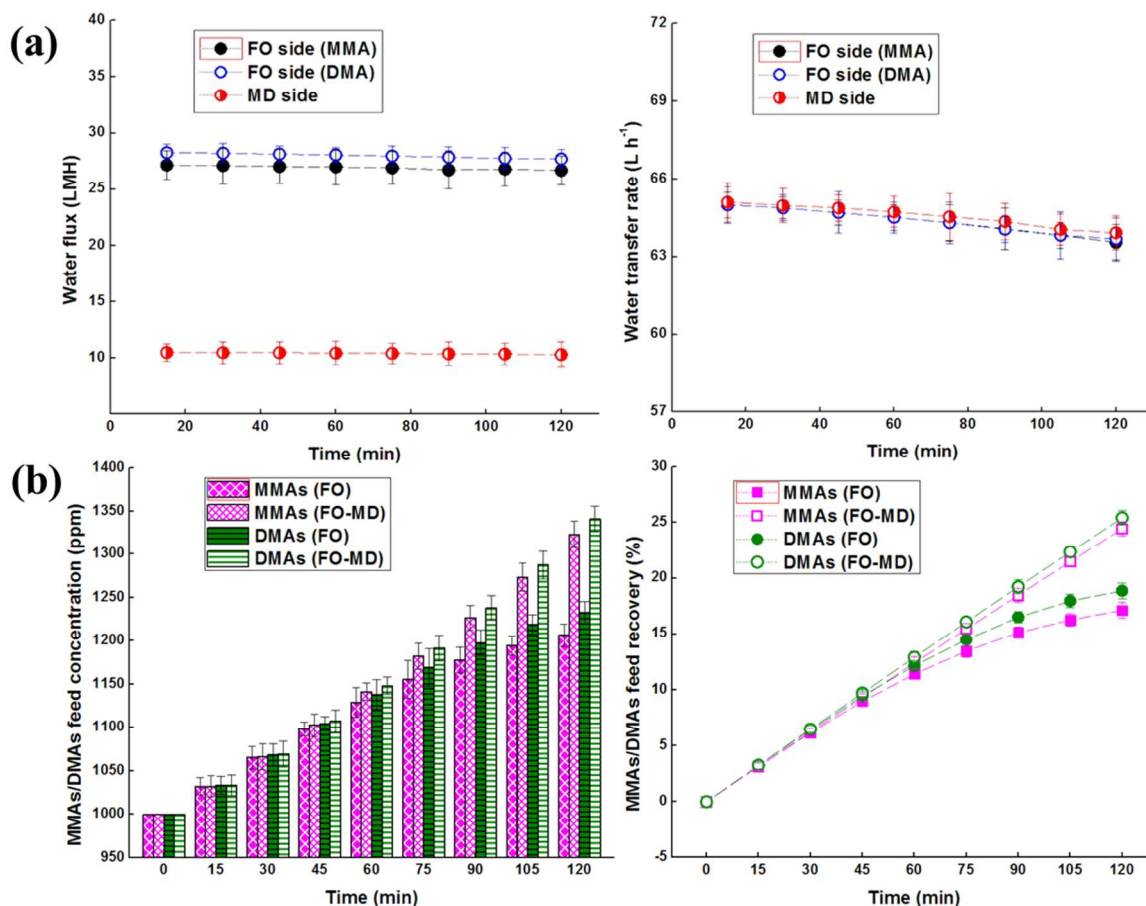
178 operation time; (b) 0 – 1000 ppm MMA or DMA in deionized water; (c) pH 3 – 11; and (d) temperature  
179 between 25 to 60 °C. Experimental conditions for each parameter are shown in the Supporting  
180 Information.

181 Different MMA concentrations did not impact on both water flux and rejection rates (Figure 4b).  
182 However, higher DMA content in the feed solution reduced the rejection rate of organic  
183 arsenicals to less than 96 %. Neutral DMA solution consists 14 % neutral species, and 86 %  
184 monovalent anions.<sup>9</sup> Higher DMA content will increase the number of neutral DMA; hence  
185 reducing the rejection rate. The ratio of neutral species to anions in MMA/DMA solutions is also  
186 sensitive to pH values (Figure 4c). As pH of a MMA feed solution changes from acidity (3) to  
187 alkalinity (11), the neutral species are converted into various anions;<sup>9</sup> hence reducing water flux  
188 due to a lower driving force attributed to enhanced osmotic feed pressures but increasing MMA  
189 rejection rates. Since DMA solution consists more neutral DMA species than MMA solution, the  
190 increase in pH from 3 to 11 will only slightly reduce water flux. Higher temperatures will also  
191 enhance the osmotic pressure differentials that consequently increase water flux (Figure 4d).  
192 Ideally, to remove 1000 ppm of MMA or DMA more effectively from water, the FO process  
193 must be conducted under neutral conditions with a higher temperature. To fully optimize the  
194 benefits of FO for removing organic arsenicals, the draw solutes must be recovered/regenerated.

195 **Regeneration of Na<sub>10</sub>-phytate Draw Solute.** Membrane distillation (MD) is a proven  
196 technology for regenerating draw solutes such as hydroacid complexes,<sup>32</sup> polyelectrolytes,<sup>15</sup> and  
197 thermosensitive polymers<sup>17</sup> from dilute FO permeate solutions. Different from FO processes  
198 where draw solution concentration significantly impacts on water flux, temperature dominates  
199 water transport in MD.<sup>33</sup> This is also observed here when aqueous solutions containing Na<sub>10</sub>-  
200 phytate at different concentrations were deployed in a single MD process using home-made

201 polyvinylidene fluoride (PVDF) hollow fiber membranes.<sup>25</sup> The increase in water flux due to  
202 increasing temperatures can be attributed to the exponential generation of higher water vapor  
203 pressures. The impacts of both Na<sub>10</sub>-phytate concentration and operation time on water flux were  
204 negligible (Figure S3).

205 By combining the FO and MD processes into a single hybrid process, we report complete  
206 recovery of Na<sub>10</sub>-phytate draw solute whilst producing 100 % water (Figure 5). The water flux of  
207 this hybrid process at 50 °C is higher than 26.0 LMH on the FO side; sufficient to handle large  
208 quantities of wastewater that are typically associated with industrial-scale operations.<sup>34-36</sup> This  
209 FO-MD hybrid technology is more efficient than single FO processes for dehydrating dilute  
210 MMA/DMA feed solutions. This is because the MD process can immediately concentrate the FO  
211 permeate consisting of Na<sub>10</sub>-phytate draw solute. The combination of our novel Na<sub>10</sub>-phytate  
212 draw solute with a hybrid FO-MD process demonstrates a simple and effective technology for  
213 removing organic arsenicals. Additional complex processes such as pre-oxidation<sup>37</sup> and  
214 operation in acidic conditions<sup>38</sup> are not required in this FO-MD process, while side reactions of  
215 MMA conversion into more toxic inorganic species<sup>39</sup> is inhibited. The combination of our novel  
216 Na<sub>10</sub>-phytate draw solute with FO-MD hybrid process surpasses the water flux and organic  
217 arsenical rejection of current technologies.<sup>1,6,8</sup>



218  
 219 **Figure 5.** (a) The water flux and water transfer rate, (b) concentrations and rejection rates of organic  
 220 arsenicals from water of a FO-MD hybrid process using 0.5 M Na<sub>10</sub>-phytate as draw solute at 50 °C. 20  
 221 °C deionized water was deployed on the MD permeate side.

222 Using a plant-derived compound, phytic acid, we designed and synthesized a novel draw  
 223 solute that is suitable for removing organic arsenicals from water in a FO-MD hybrid process.  
 224 The presence of hydrophilic functional groups arranged in a three-dimensional configuration  
 225 around an aromatic carbon ring can form supramolecular structures through hydrogen bonds with  
 226 water molecules that prevent reverse diffusion during FO processes. This draws water across a  
 227 TFC-PES hollow fiber membrane at rates that can handle industrial-scale quantities of  
 228 wastewater. The regeneration of the novel Na<sub>10</sub>-phytate draw solute is optimized using an in-line  
 229 MD process; streamlining the draw solute recovery process with minimal energy consumption.



230 Phytate-based draw solutes can be potentially deployed for the removing other types of  
231 contaminants during water treatment and are especially suitable for protein enrichment. The  
232 negligible reverse diffusion of Na<sub>10</sub>-phytate in FO can avoid denaturation of impurity-sensitive  
233 proteins and produce high-quality products.

## 234 ■ AUTHOR INFORMATION

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## 242 ■ ASSOCIATED CONTENT

243 Supporting Information Available

244 Materials; syntheses and characterizations of Na<sub>10</sub>-phytate; the physicochemical properties of  
245 Na<sub>10</sub>-phytate solutions; FO processes; the preparation and analyses of MMAs and DMAs  
246 solutions; the regeneration of Na<sub>10</sub>-phytate; molecular structures of MMAs and DMAs; the TGA  
247 spectrum; weight losses of Na<sub>10</sub>-phytate in TGA measurements; relative viscosity of Na<sub>10</sub>-  
248 phytate and phytic acid; osmotic pressure of Na<sub>10</sub>-phytate, phytic acid and NaCl; Supermolecular  
249 network and size distribution of Na<sub>10</sub>-phytate in the aqueous solution.

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