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## Inter-layer free Cobalt-doped Silica Membranes for Pervaporation of Ammonia Solutions

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21 **Abstract**

22 This study demonstrated the application of a new type of interlayer-free cobalt-doped silica  
23 membrane in treating ammonia solutions by pervaporation applied towards wastewater treatment. For  
24 enhanced hydrothermal stability, cobalt-doped silica (CoSi) membranes with increasing cobalt  
25 concentrations from 1 to 35 mol% were prepared and evaluated, namely CoSi-1, 5, 20 and 35. These  
26 membranes exhibited high water fluxes of  $66 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$  for CoSi-1 and  $15.5 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$  for CoSi-35 at 45  
27 °C. The fluxes of the membranes decreased with increasing cobalt concentration; while the rejection  
28 to total nitrogen (TN, ammonia nitrogen) increased and hence allowed selective passage of water  
29 molecules. Enhanced thermostability was observed for the membranes, particularly CoSi-35 that  
30 exhibited TN rejection up to 99% at high temperature of 65 °C and highly alkaline environment  
31 (pH>10). Also, the CoSi-35 membrane showed stable performance in treating ammonia present in  
32 industry wastewater by achieving stable TN and mineral rejections of 97% and 99%, respectively.  
33 Fouling was observed and confirmed by SEM morphological analysis and EDX elemental inspection.  
34 The results indicated the deposition of low solubility salts such as  $\text{CaSO}_4$ .

35

36 **Keywords:** Interlayer-free; cobalt-doped silica membrane; pervaporation; TN rejection;  
37 thermostability.

38

## 39 **1. Introduction**

40 Ammonia nitrogen is a common pollutant in various wastewaters including municipal and industry  
41 effluents. The discharge of wastes containing ammonia cause eutrophication in natural waterways  
42 and is regarded highly toxic to aquatic life. Its presence in the sewer also poses a risk to sewage  
43 workers. Therefore, the removal of ammonia is essential for protecting the environment and human  
44 health. In wastewater treatment plants, the aerobic process is widely used to convert ammonia  
45 nitrogen to nitrogen gas assisted by intensive aeration, where the latter accounts for about 80% of the  
46 overall electrical energy use in the plant [1]. Hence, a more efficient approach of nitrogen removal is  
47 required to reduce the energy consumption. This includes alternative biological de-ammonification  
48 such as anammox [2] and novel physical ammonia capture process [3].

49 In recent years, membrane processes have been considered as an effective and physical means to strip  
50 ammonia from aqueous solutions, including the use of polymeric membranes in membrane contactors  
51 [4, 5] and polymeric membrane distillation (MD) [6-9], as well as inorganic membranes in  
52 pervaporation (PV) [10, 11]. Nevertheless, only a handful studies available in literature have explored  
53 the mechanisms of ammonia separation in membrane technology in aqueous environment. Through  
54 conventional porous hydrophobic polymeric membranes (pore size in  $\mu\text{m}$ ), a typical MD process  
55 works according to distillation theory and strips the volatile ammonia from the feed solution with the  
56 permeate side under vacuum. Previous studies showed that ammonia could be concentrated to a  
57 higher strength, i.e., >12 times of its feed concentration [10], and could be recycled as fertilizer  
58 component or used as processing chemicals. A recent study reported the role of water chemistries  
59 leading to a successful ammonia removal by vacuum MD (VMD) from real industry wastewaters  
60 under real industry settings without pH adjustment (pH 6.0-8.0) [12].

61 Most work on ammonia separation from aqueous solution focusses on use of hydrophobic polymer  
62 membranes that work by distillation. Meanwhile inorganic membranes with molecular sieving pores  
63 may offer a suitable alternative to a more tailored separation [10]. Inorganic silica membrane are

64 unstable in water, though its applications in water processing were reported a decade ago. These  
65 initial reports stemmed from embedding carbon templates [13] metal oxides [14] into silica  
66 membranes. Carbon templates improved the hydrophobicity of silica membranes [15] and provided  
67 a hindrance for the diffusion of unstable silanol (Si-OH) groups [16], while metal oxides greatly  
68 improved hydrothermal stability [17]. Recent advances have shown that these hybrid silica  
69 membranes can be prepared without interlayers [18-20] or with different silica precursors [20] instead  
70 of the conventional silica membranes with interlayers, thus reducing the production costs of silica  
71 membranes. A major advantage of silica membranes is the flexibility of the sol-gel method to tailored  
72 pore sizes to subnano-scale. Although the majority of the previously reported work on silica derived  
73 membranes has been focused on desalination, we postulate that silica membranes can also process  
74 liquids containing ammonia. In a previous study, a cobalt-doped molecular sieve silica membrane  
75 was found to have high ammonia selectivity up to 60 times [10]. However, rapid material degradation  
76 was observed due to the exposure to hydrothermal conditions, i.e., up to 90 °C aqueous environment.  
77 Similar degradation was reported to organosilica membrane, though the instability was attributed to  
78 the  $\gamma$ -alumina interlayer of the substrate[11]. Thus, to overcome material stability problem under  
79 hydrothermal conditions and basic or alkaline water chemistries, it is proposed that the new age silica  
80 membrane with alternative or no interlayer materials are needed.

81 Therefore, we selected interlayer free cobalt oxide silica membranes (CoSi) and investigated their  
82 performance for the purification of ammonia contaminated wastewaters. Particularly, we are  
83 interested in the correlations between membrane materials and performance. For instance, we  
84 evaluate the effect of cobalt concentration embedded in the silica membrane against performance  
85 parameters such as flux and rejection to total nitrogen. The membrane stability and performance are  
86 also investigate as a function of the pH condition of the aqueous solution. Furthermore, the CoSi  
87 membranes are then exposed to real industrial wastewater from an ion exchange regeneration column  
88 where their performance is tested in terms of fouling and stability in water purification.

89

## 90 **2. Experimental**

### 91 *2.1 Membrane Materials and Characterisation*

92 A series of CoSi membranes were prepared using a dual acid-base catalyzed sol gel and interlayer  
93 free approach reported by Elma et al.[21]. In this method, cobalt nitrate hexahydrate was used as a  
94 cobalt precursor, which was added into the silica sol after 3 hours of refluxing. The mixture was  
95 stirred for an additional 45 min to ensure homogeneity. The molar ratio of cobalt oxide in the silica  
96 sol was varied from 0 to 35 mol%, corresponding to pH range of 6 to 4.44 being above the isoelectric  
97 point (pH 1-3) of silica particles. The mixed sol was dried in an oven at 60 °C for 24 hours to obtain  
98 dried **gels**, which was then grounded into powder and calcined at 600 °C for 4 hours producing the  
99 CoSi **gel**. Hence, four membrane with different cobalt content of 1, 5, 20 and 35 mol% by dip-coating  
100 the **gel** four times onto the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> tubular substrate (Ceramic Oxide Fabricators, Australia) with  
101 macro-porous pore structure of 100 nm on average and outer diameter of 10 mm. The cross-section  
102 and surface of the virgin and used CoSi membranes were examined using a field emission scanning  
103 electron microscopy (FESEM). The surface chemistry and elemental information due to foulant  
104 deposition was quantified by a JEOL2100 microscope equipped with energy-dispersive x-ray  
105 spectroscope (EDS).

106

107

### 108 *2.2 Membrane performance tests*

109 Pervaporation experiments were performed using the setup described in previous work [10, 11], in  
110 which the membrane was submerged into a feed solution. The membrane tube, with an outer surface  
111 area of 17 cm<sup>2</sup>, was blocked at one end and connected to vacuum line on the other end at an absolute  
112 pressure of 100–300 Pa. The feed solution was mixed homogeneously using a stirrer (stirring speed  
113 range: 300-1000 rpm) and heated to 35–65 °C. Two liquid nitrogen cold traps were placed along the

114 vacuum line to capture the vapour generated at 60 min intervals. During batch operation with small  
115 membrane area, the feed concentration was maintained constant by continuously supplying fresh feed.  
116 Tests under each condition were repeated three time (1-hour each) to ensure reproducibility. Both  
117 synthetic and industrial water samples were tested. After industrial sample testing, membrane  
118 cleaning was conducted with base and acid solutions separately, *i.e.*, 0.5% NaOH and 1 % HCl.

119

### 120 2.3 Test solutions

121 Synthetic feed solutions were prepared by adding 300 mg/L (equivalent to 280 mg-N/L) ammonia  
122 ammonium hydroxide (28-30% NH<sub>3</sub>, Sigma-Aldrich) and 500 mg/L sodium chloride (NaCl) into  
123 deionized (DI) water, at both pH 7 and 11 adjusted by 2M HCl solution. Sodium chloride was added  
124 to maintain a realistic electrolytic balance in the solution for comparison with industry samples. A  
125 model industry wastewater (pH 7.5) was obtained from an ion exchange (IX) regeneration process  
126 from an industrial demineralisation plant. This sample was tested only at 45 °C, which represents the  
127 readily available low-grade waste heat from industry [22].

128

### 129 2.4 Sample Analysis

130 The total nitrogen concentration (indicative of NH<sub>3</sub> concentration) of the feed and permeate samples  
131 was measured using the Total Nitrogen unit (Model no: TNM-1) of the Shimadzu TOC/TN analyser,  
132 followed the previous procedure reported in elsewhere [10]. All samples were analysed for elements  
133 (K, Mg, Na, Co, Si, P and S for sulphate) representing cations (anion for sulphate) by ICP-OES. Total  
134 dissolved solid (TDS) and solution pH were measured by a Hach portable meter with dual  
135 conductivity and pH probes. The composition of the fouling layer was examined through quantifying  
136 the elemental concentrations in the washed solutions.

137

138 2.5 Performance calculations

139 To analyse the practical separation of the membrane, the rejection of components such as total  
140 nitrogen (TN or ammonia nitrogen) and minerals is defined as,

141 
$$rejection = 1 - \frac{c_p}{c_f} \quad (1)$$

142 where  $C$  denotes the concentration of components,  $p$  and  $f$  represent the permeate and feed sides of  
143 the membrane, respectively.

144

145 To reveal the intrinsic separation properties of the cobalt-doped silica membrane, the permselectivity  
146 of ammonia ( $i$ ) and water ( $j$ ),  $\alpha_{ij}$ , is used. It is defined as the ratio of the molar permeabilities or  
147 permeance of components  $i$  and  $j$  through the membrane, as [23]:

148 
$$\alpha_{ij} = \frac{P_i^G}{P_j^G} = \frac{P_i^G/\ell}{P_j^G/\ell} \quad (2)$$

149 where  $P_i^G$  is the membrane gas permeability of component  $i$  ( $\text{cm}^3(\text{STP})\cdot\text{cm}/\text{cm}^2\cdot\text{s}\cdot\text{cmHg}$ ) and  $\ell$  is the  
150 membrane thickness.  $P_i^G/\ell$  is the permeance of component  $i$ . It can be defined as the component flux  
151 normalized for driving force across the membrane:

152 
$$\frac{P_i^G}{\ell} = \frac{D_i \cdot K_i^G}{\ell} = \frac{j_i}{p_{io} - p_{il}} \quad (3)$$

153 where  $D_i$  is the membrane diffusion coefficient ( $\text{cm}^2/\text{s}$ ) of component  $i$ ;  $K_i^G$  ( $\text{cm}^3(\text{STP})/\text{cm}^3\text{cmHg}$ ) is  
154 the sorption coefficient.  $j_i$  is the molar flux of component  $i$  with unit of  $\text{cm}^3(\text{STP})/\text{cm}^2\cdot\text{s}$ .  $p_{io}$  and  $p_{il}$   
155 are the respective partial pressure of the component  $i$  on either side of the membrane (surface  $o$  facing  
156 the feed solution and  $l$  facing the permeate). The partial pressure of the feed side  $p_{io}$  can be obtained  
157 based on Henry's law [23]:

158 
$$p_{io} = H_{io} x_{io}^L \quad (4)$$

159 where  $H_{io}$  is the Henry's law constant [24] indicating the ammonia-ammonium equilibrium  
160 relationship,  $x_{io}^L$  is the mole fraction of the component  $i$  in the feed liquid.  $p_{il}$  is calculated based on

161 the vacuum pressure of pervaporation and permeate concentration. The  $\alpha_{ij}$  is indicative of the actual  
162 separation function of the membrane excluding the effect of process driving force and volatility  
163 difference, i.e., partial vapour pressure. An  $\alpha_{ij}$  value of 1.0 will be expected if the membrane does  
164 not contribute to separation and is instead working completely by distillation, for which Table A1 is  
165 provided in the Supporting Information containing the respective partial pressure of water and  
166 ammonia in the temperature range of 35 to 65°C at pH 11. A value of below 1.0 indicates water  
167 selective feature of the membrane; otherwise ammonia selective when  $>1.0$ . In this paper, the symbol  
168  $\alpha_{NH_3/H_2O}$  is used for discussions.

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### 171 3. Results and discussion

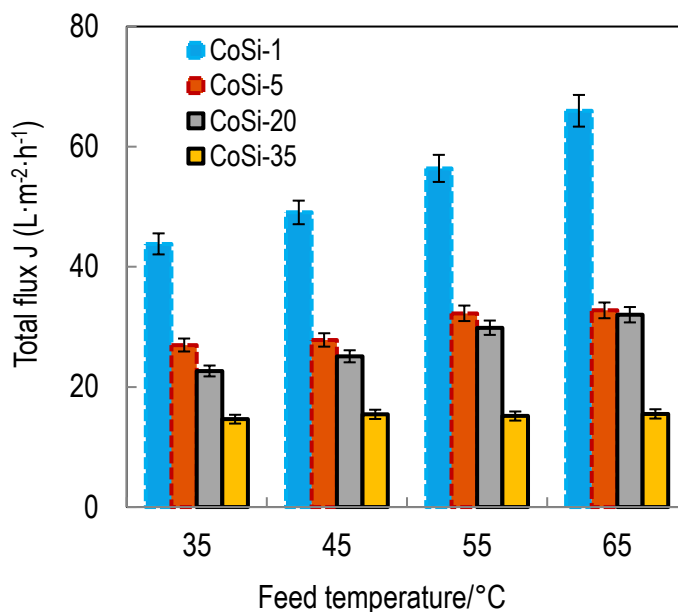
#### 172 3.1 Separation performance of synthetic solutions

173 The effect of cobalt content in the membrane (in mol %) was investigated through testing a pH 7.0  
174 synthetic solution containing 500 mg/L sodium chloride and 280 mg-N/L. The results of total  
175 membrane flux and total nitrogen (i.e., TN or ammonia) rejection at varying feed temperatures are  
176 shown in Fig. 1. It is observed in Fig. 1a that the total flux decreases with increasing cobalt content.  
177 For example, at feed temperature of 65 °C, the CoSi-1 membrane reached fluxes of 66 L·m<sup>2</sup>·h, which  
178 consistently reduced to the the lowest flux of 15 L·m<sup>2</sup>·h<sup>-1</sup> for the CoSi-35 membrane. The total flux  
179 increased for all membranes with increasing temperature from 35 °C to 65 °C, except for CoSi-35,  
180 whose flux remained relatively constant in the given temperature range. The increase in flux is mainly  
181 attributed to an increase in the driving force, which is a function of the vapour pressure determined  
182 by the temperature gradient across the membrane. While the insignificant effect of temperature on  
183 the flux of CoSi-35 could be due to the tight pore structure at high Cobalt content as compared to the  
184 others.



185 Fig. 1b shows that the TN rejection of all CoSi membranes increases with increasing cobalt  
186 concentration. Of particular attention, the membrane with the highest content of Co 35 mol%,  
187 delivered a stable TN rejection for all tested temperature, which actually increased from 94 to 99%  
188 as the temperature was raised from 35 to 65 °C, respectively. Contrary to this CoSi-1 and CoSi-5 TN  
189 rejection decreases drastically with increasing temperature. This loss of performance is associated  
190 with the deterioration of these low Co content silica membranes, due to hydrothermal instability of  
191 the high silica content. The CoSi-20 membrane showed a reasonable stability which deteriorated at  
192 the highest testing temperature of 65 °C. These results clearly indicate that role played by high content  
193 of cobalt oxide embedded in the silica matrix, thus conferring higher hydrothermal stability otherwise  
194 not available in pure silica or low Co content silica membranes.

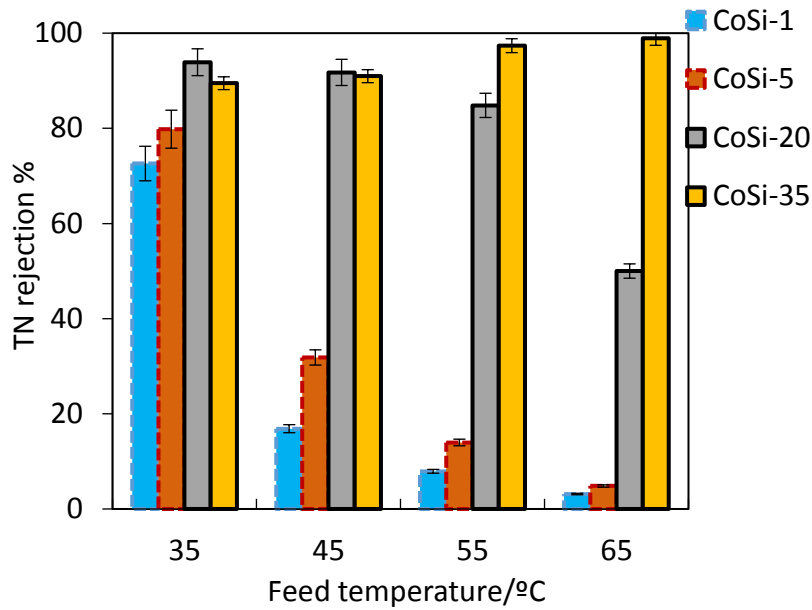
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(a) Total flux



(b) TN rejection

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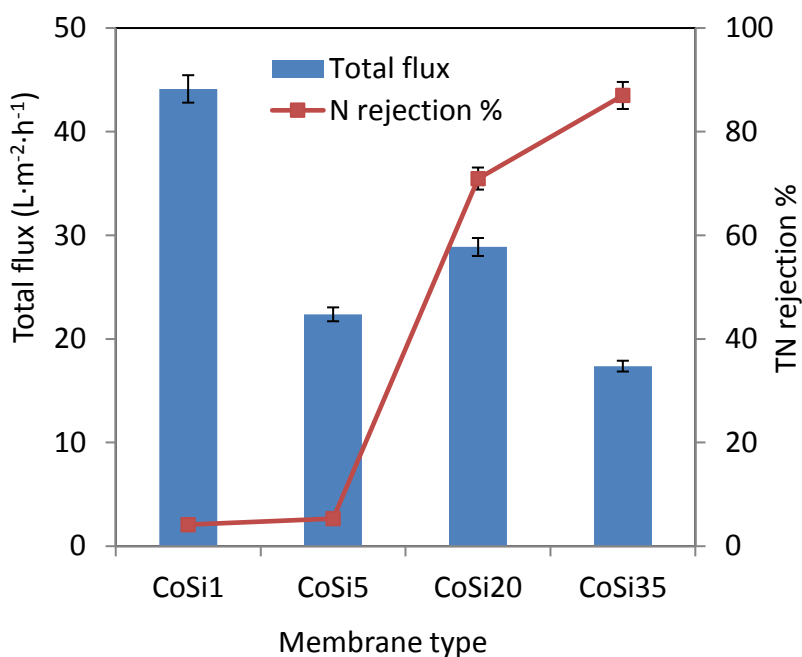
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201 Fig. 1 Total flux  $J$  and TN rejection rate of four cobalt doped interlayer free silica membranes with  
 202 pH 7 synthetic ammonia solution in pervaporation (initial  $TN=280$  mg-N/L,  $T_f=35-65^\circ\text{C}$ ,  $P_v =100-$   
 203 300 Pa absolute, 3-hour PV test conducted under each condition)

204 The results in Fig. 1 confirms that the CoSi-35 membrane could be suitably applied to treat industry  
 205 samples in similar pH conditions (6.0-8.0), however the proportion of free volatile ammonia is low,  
 206 i.e. 2% at pH 7.0. So to better explore the ammonia rejecting property of the membranes, tests were  
 207 conducted at higher pH of 11.0 as shown in Fig. 2, where more free volatile ammonia is present thus  
 208 better confirming this effect of the silica material prior to testing on real industry samples. It was  
 209 found that the membrane flux decreases with increasing cobalt concentration, except for CoSi-5 that  
 210 showed a lower flux than that of CoSi-20. This may be related to its microporosity with low pore  
 211 volume, as observed in a previous study [21]. Also, compared to the flux results at  $65^\circ\text{C}$  and pH 7 in  
 212 Figure 1, it is observed that the flux for each CoSi membrane at pH 11 decreases or remains  
 213 unchanged in Figure 2. This is because for these membranes, which exhibit water selectivity, the  
 214 vapour flux is strongly affected by the fraction of free ammonia in the solution. Although ammonia

215 has a relatively small chance of entering the membrane pores, it may still act to inhibit water flux at  
216 the pore surface. Similar to the observation from the pH 7.0 solution testing (Fig. 1), the TN rejection  
217 (in %) increases with increasing cobalt concentration, i.e., 4% and 87% for the CoSi-1 and CoSi-35  
218 membranes, respectively. Given the larger fraction (99.8%) of free ammonia to total ammonia  
219 nitrogen in the pH 11.0 feed solution, the current results have shown consistent separation preference  
220 of the membrane towards water. Also, the stable performance of CoSi-35 has indicated the potential  
221 of cobalt surface modified silica membranes for treating wastewater containing ammonia nitrogen  
222 under alkaline and hydrothermal environment, which was challenging for silica membrane with  $\gamma$ -  
223 alumina interlayer [11].



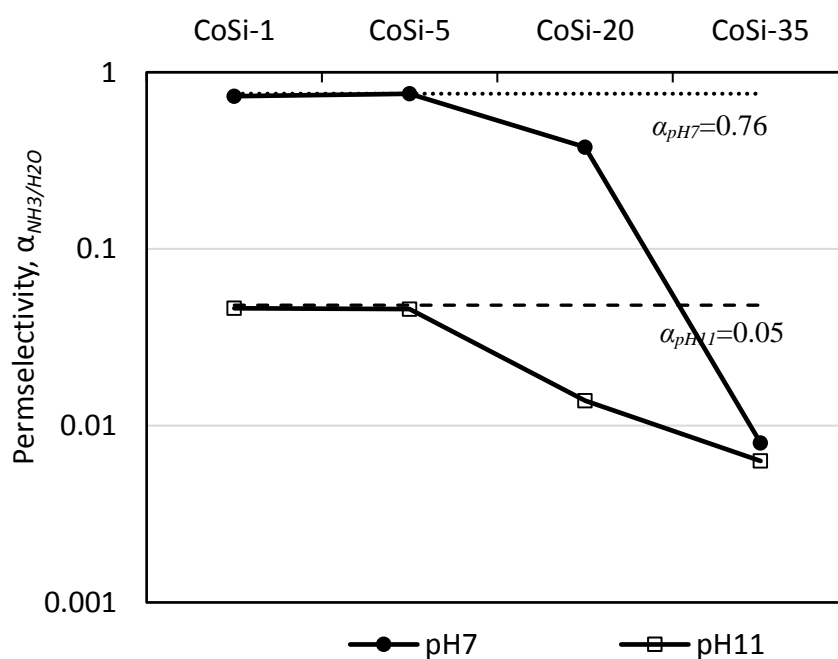
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225 Fig. 2 Total flux  $J$  and TN rejection % of four Cobalt doped interlayer free silica membrane in  
226 synthetic ammonia solution with pH 11.0 (initial TN=280 mg/L,  $T_f=65^\circ C$ ,  $P_v=100-300$  Pa absolute,  
227 membrane area  $A=0.0017m^2$ )

228

229 The overall results of good TN rejection obtained by the cobalt-dope silica membranes, particularly  
230 CoSi-35, has indicated effective separation between ammonia and water. To reveal the intrinsic

231 separation of the membranes, the molar permselectivity,  $\alpha_{NH_3/H_2O}$  (Equation (2)), was calculated for  
 232 the four CoSi membranes based on the performance at 65°C testing with pH 7.0 (Fig. 1) and pH 11.0  
 233 (Fig. 2) synthetic solutions. The  $\alpha_{NH_3/H_2O}$  results are plotted in logarithmic scale, as shown in Fig. 3,  
 234 with the  $x$ -axis starting from 1.0 where distillation separation effect for ammonia-water system is  
 235 dominant. Two dashed lines for the respective pH conditions were set at  $\alpha_{pH7}=0.76$  and  $\alpha_{pH11}=0.05$   
 236 based on the permselectivity calculation where no separation occurs. It was found that the  $\alpha_{NH_3/H_2O}$   
 237 values of all membranes at both pH values are below the respective benchmark lines, indicating truly  
 238 water selective (or ammonia rejective) feature. Although high pH is favourable for the release of  
 239 volatile ammonia (e.g., 99.8% of TN as free ammonia at pH 11.0 [12]) from its aqueous solution, the  
 240 results of both pH have shown consistent separation behaviours of the CoSi membranes, particularly  
 241 at high pH of 11 the  $\alpha_{NH_3/H_2O}$  is much below 1.0. Also, the ammonia-water separation function is  
 242 greatly enhanced with increasing cobalt concentration from 1 to 35 mol%, as indicated by the rapidly  
 243 decreasing trend lines of the  $\alpha_{NH_3/H_2O}$  at both pH conditions. **The corresponding permeance data**  
 244 **(Equation 3) of the membranes at both pH 7 and 11 is provided in the supporting materials as Fig.**  
 245 **A1, where the respective permeance of water and ammonia show consistent trends of the separation**  
 246 **mechanism of the CoSi membranes.**

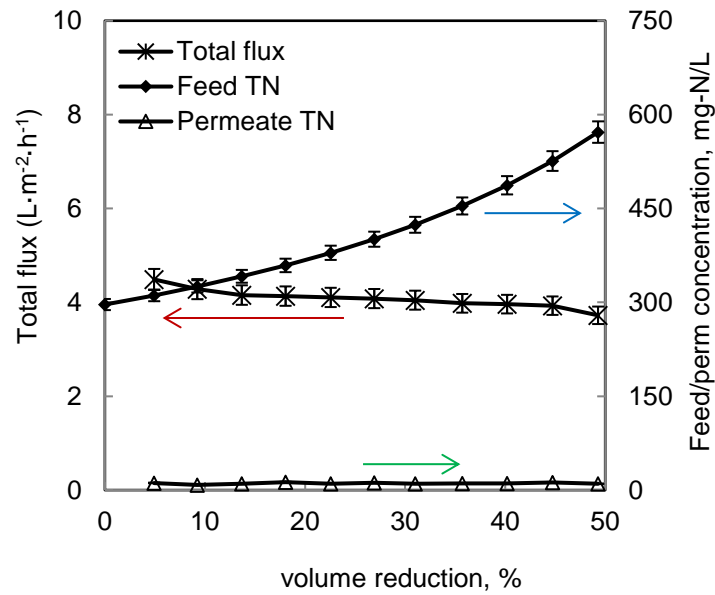


247

248 Fig. 3 Comparison of permselectivity  $\alpha_{NH_3/H_2O}$  at various CoSi ratio (initial TN=280 mg/L,  $T_f=65^\circ\text{C}$ ,  
249 pH=7.0&11.0,  $P_v = 100\text{-}300$  Pa absolute, membrane area  $A=0.0017\text{m}^2$ ). Dashed lines indicate no  
250 separation (feed concentration = permeate concentration)

### 251 3.2 Membrane performance in industry wastewater testing

252 The composition of the industry wastewater is given in Table 1. Fig. 4 shows total membrane flux,  
253 respective feed and permeate ammonia concentrations (as TN in mg-N/L) as a function of volume  
254 reduction % (or water removal). It was found that the total flux decreases from 4.9 to 3.7  $\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ ,  
255 50 vol% volume reduction. The magnitude of flux for the industry sample was four-fold lower than  
256 that of the synthetic solution ( $17.5 \text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ ) containing only sodium chloride and ammonia. This is  
257 due to the increase TDS leading to lower vapour pressure and the presence of sparsely soluble salts  
258 such as calcium sulphate, which could have strong impact on the membrane flux behaviour. The flux  
259 decline has pointed towards potential fouling problems. The TN concentration of the feed increases  
260 gradually by two-fold at 50 vol% volume reduction due to the ammonia rejective function of the  
261 membrane, i.e., from the initial concentration of 296 mg-N/L to 573 mg-N/L. While the permeate TN  
262 remains constantly below 10 ppm, corresponding to 97% rejection. The rejection to sodium salt is  
263 also above 99%, as indicated in Table 1. Hence, similar to the synthetic solution testing (Figs. 1 and  
264 2), both minerals and ammonia in the industry sample were well retained in the retentate stream,  
265 regardless of solution pH.



266

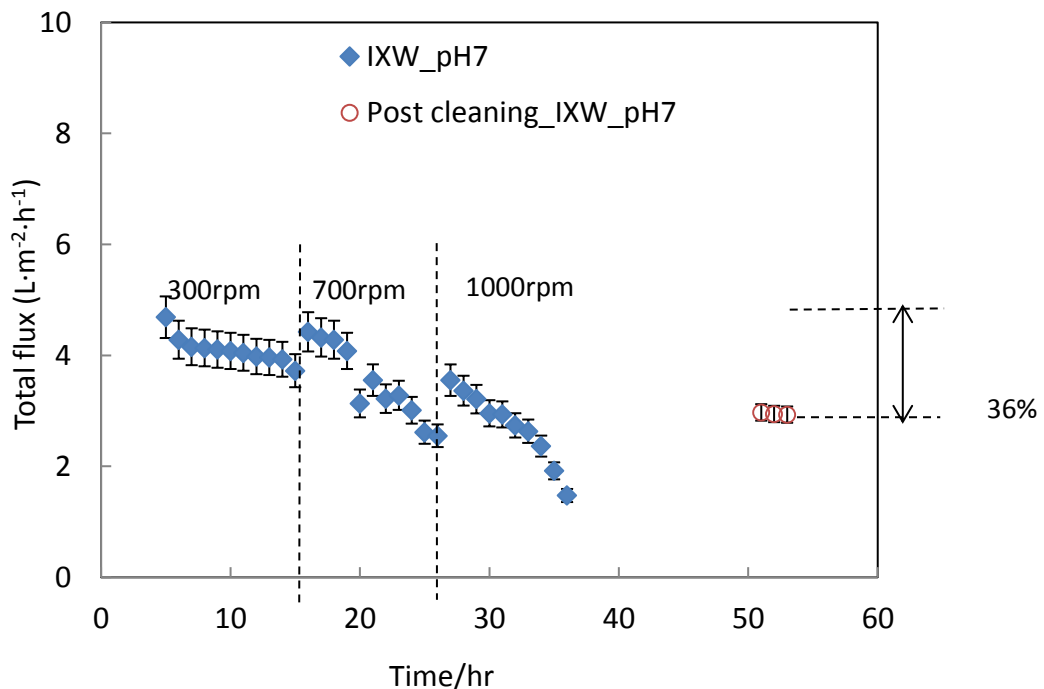
267 Fig. 4 Membrane performance of CoSi-35 using industry wastewater (initial ammonia concentration  
 268 as 296 mg-N/L, pH=6.93,  $T_f=45^\circ\text{C}$ , vacuum pressure = $0.2\pm 0.1$  kPa absolute, stirring intensity  
 269 300rpm, membrane area  $A=0.0017\text{m}^2$ )

270

271 To further investigate the flux decline from industry sample testing (as shown in Fig. 4), the  
 272 experiments with CoSi-35 membrane were repeated in a longer run of 60 hours including pure water  
 273 testing, before and after chemical cleaning. The results are shown in Fig. 5. The testing on industry  
 274 sample last for 10 hours in the first stage, the initial flux for the wastewater was  $4.7 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ . Despite  
 275 the temporary increases in flux by increasing stirring speed during the test from 300rpm to 700rpm,  
 276 and then to 1000rpm, **inevitable flux decline to  $1.5 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$  was observed** by the end of the 10 hour  
 277 run. **Thus the attractive force between the fouling species and membrane may not have been overcome**  
 278 **over longer term by higher stirring speed.** The **eventual** flux decline is possibly due to membrane  
 279 fouling **induced by concentration polarization** and subsequent pore blockage when treating industry  
 280 effluent.

281 To reverse possible fouling, the membrane was cleaned with acid (0.5 wt%) and alkaline (1.0 wt%)  
 282 solutions. Based on the flux data before and after cleaning in Table 2, the **testing with pure water was**

283 used to benchmark of membrane performance and it shows that in the post-cleaning stage the flux  
 284 was successfully restored to 73% of the original flux of the fresh membrane, indicating the partial  
 285 removal of contaminants and effectiveness of membrane cleaning. Similarly, the subsequent test on  
 286 the wastewater gave partially restored flux as 64% of the original value ( $4.7 \text{ L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ ). Throughout  
 287 the 60-hour testing, the membrane integrity was maintained exhibiting good hydrothermal stability  
 288 of the membrane working under industrial water chemistry. The rejection of TN and other elements  
 289 remained relatively stable throughout the operation, as shown in Table 1, in which the dissolved solids  
 290 including Na, Ca, Mg, P and K salts were rejected more than 99% and the TN rejection was 97%.  
 291 The rejection of total organic (TC) is lower than 50% due to the presence of inorganic carbon (as  
 292 carbonic acid or bicarbonate) and low molecular weight organic carbon in the feed that easily pass  
 293 through the membrane. Consistent with previous tests (Figs. 1 and 2), the presence of ammonia in the  
 294 permeate is minimal. However, the presence of  $\text{Ca}^{2+}$  and  $\text{SO}_4^{2-}$  in the solution indicated the fouling  
 295 potential, which is worth further investigation.



296

297 Fig.5 Membrane flux of CoSi-35 with industrial wastewater pH 7.4: (◆) new membrane ; (○) after  
 298 chemical cleaning (initial TN=296 mg/L,  $T_f=45^\circ\text{C}$ , vacuum pressure =100-300 kPa absolute,  
 299 stirring speed: 300, 700 and 1000rpm, membrane area  $A=0.0017\text{m}^2$ )  
 300

301 Table 1 Rejection data of various species in industry wastewater sample testing throughout 60-hour  
 302 operation

Component	Feed concentration (mg/L)	Permeate concentration (mg/L)	Rejection (%)
TN (mg-N/L)	296	10	97
TC(mg-C/L)	16	9.6	40.3
K <sup>+</sup>	3.7	<0.01	99.7
Na <sup>+</sup>	538	<0.1	99.9
P	3.36	<0.01	99.9
Ca <sup>2+</sup>	57.2	<0.01	99.9
Mg <sup>2+</sup>	6.9	<0.01	99.9
S	4.42	<0.01	99.9

303

304 Table 2 Comparison of DI water and industry sample initial and final fluxes, and flux recovery after  
 305 cleaning ( $T_f=45^\circ\text{C}$ , vacuum pressure =100-300 kPa absolute, each test lasted for 3 hours, membrane  
 306 area  $A=0.0017\text{m}^2$ )

Feed	Initial flux (new membrane) $\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$ ,	Final flux (used membrane, before clean), $\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$	Post cleaning flux, $\text{L}\cdot\text{m}^{-2}\cdot\text{h}^{-1}$	Flux restored %, post cleaning
DI water	18.2	4.5	13.3	73%
Industry wastewater	4.9	1.5	3.1	64%

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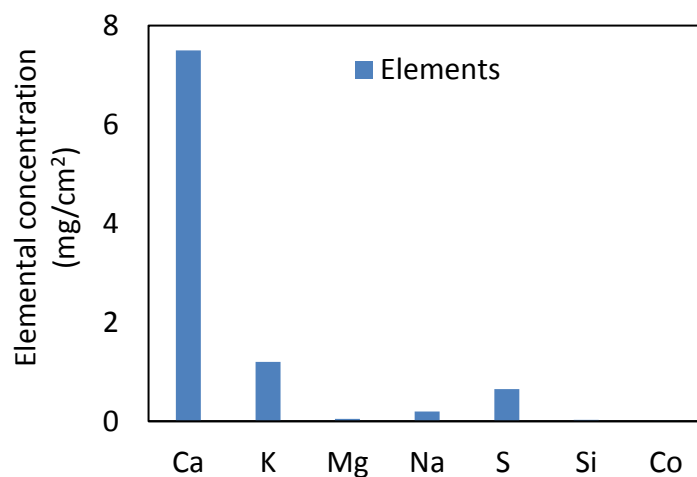
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309

310 Correspondingly, the elemental analysis of the cleaning solutions (acid and base) was measured by  
 311 ICP-OES. The results are presentd in the bar chart in Fig. 6. It was found that the concentrations of



312 the Ca are highest compared to other cations, indicating the precipitation of Ca salts on the membrane  
313 surface, which could be prevented through various approaches [25], e.g., by improving the flow  
314 dynamics to reduce surface polarization or using conventional pretreatment means such as anti-  
315 scalant or microfiltration membrane prior to the CoSi membranes for ammonia separation. The  
316 presence of  $\text{SO}_4^{2-}$  is indicated by the elemental analysis of S. Also, there was some amount of Si and  
317 Co (in minor concentrations of 0.03 and 0.009  $\text{mg}/\text{cm}^2$ , respectively) present in the cleaning solutions.  
318 The Si could be related to its existence in the water sample (in 0.72  $\text{mg}/\text{L}$ ); while the Co could be due  
319 to slight dissolution from the membrane coating into the cleaning chemicals due to the use of basic  
320 solution that creates high pH environment. This means that future cleaning strategies should be  
321 adjusted to avoid dissolution of both Si and Co.

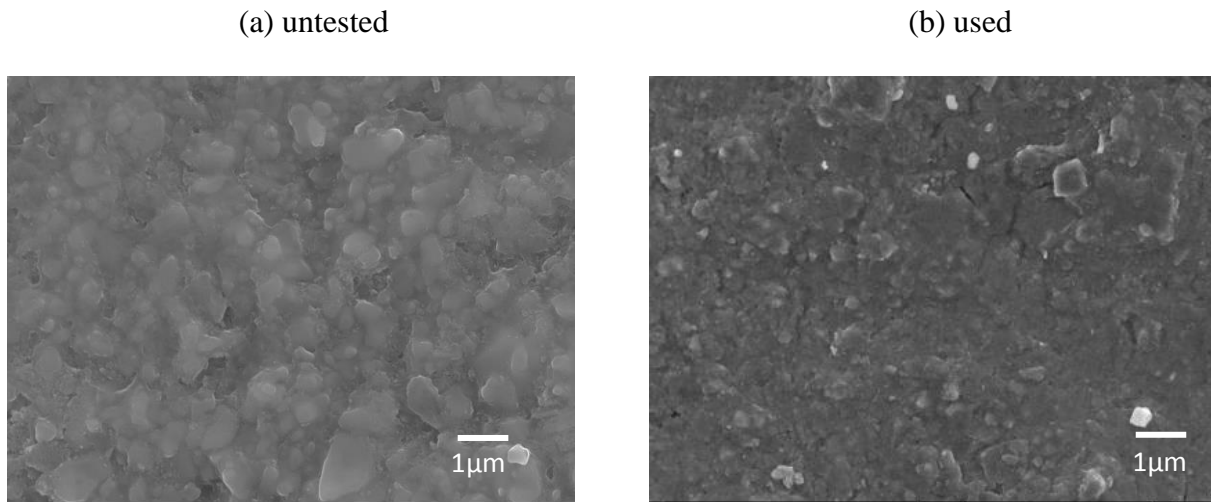


322  
323 Fig. 6. Mineral content of cleaning solutions (acid and based added together) after 30h industry  
324 sample testing

325  
326 According to the cross-section images of the CoSi membranes were shown in the previous work [21],  
327 where no distinct layers between the cobalt coating and the  $\alpha\text{-Al}_2\text{O}_3$  substrate, the infiltrated sol layer  
328 into the substrate is up to  $10\mu\text{m}$ . This work only shows the SEM images of the surface morphologies  
329 of the untested (intact) and used CoSi-35 membrane after industry sample testing, as presented in Fig.

330 7. The membrane surface which was in direct contact with the feed solution showed some cracks to  
331 appear as a result of testing.

332



333

334 Fig. 7 SEM images of outer surface of CoSi-35 membrane before (untested) and after (used)  
335 pervaporation at 10,000x magnification with a scale bar of 1 μm

336

337 The cleaned CoSi-35 membrane was also inspected by EDX to reveal the elemental composition of  
338 the untested and cleaned membrane surface. The results are shown in Table 3. The untested membrane  
339 contained only C, O, Al, Si and Co representing aluminium oxide and surface coating materials. The  
340 Co mol% is 32% which is close to the designed concentration of the cobalt oxide silica sol gel during  
341 membrane fabrication, i.e., 35mol%, as reported in previous work [21]. For the chemically cleaned  
342 membrane, additional elements such as Na, Mg, K, Ca and Cl appeared. This is probably due to  
343 mineral deposition during pervaporation.

344

345

346 Table 3. SEM-EDS analysis of membrane outer surface before and after filtration of industry  
 347 wastewater

Atom	Energy (keV)	Atomic concentration (%) untested membrane	Atomic concentration (%) Tested and cleaned membrane
C (K)	0.3	11.7	9.9
O (K)	0.5	54.2	46.8
Al (K)	1.5	27.7	32.5
Si (K)	1.7	4.3	2.1
Co (K)	6.9	2.0	5.3
Na (K)	1.0	--	1.1
Mg (K)	1.3	--	0.7
Cl (K)	2.6	--	1.2
K (K)	3.3	--	0.1
Ca (K)	3.7	--	1.1
<b>Total</b>		<b>100</b>	<b>100</b>

348

349

#### 350 4. Conclusions

351 This study has demonstrated the application of a new type of interlayer-free cobalt-doped silica  
 352 membrane in treating ammonia containing wastewaters via pervaporation. The initial assessment  
 353 using synthetic ammonium solutions showed that the interlayer-free membranes exhibited superior  
 354 water flux and high rejection to ammonia, except for the membranes had low cobalt content such as  
 355 CoSi-1 and CoSi-5 that failed at 65 °C and pH 11.0. Good hydrothermal stability of the cobalt-doped  
 356 membranes was observed as the cobalt ratio increased in the cobalt silica coating. It was further  
 357 demonstrated that the best performed CoSi-35 membrane was able to purify an industry wastewater,  
 358 while the TN rejection remained high at 97% and rejection to minerals was above 99%. Although  
 359 flux decline was detected over time, chemical cleaning was able to partially restore the membrane  
 360 performance. Membrane autopsy results indicated the fouling propensity of the membrane that is

361 susceptible to inorganic deposition particularly due to the presence of sparsely soluble salts such as  
362 CaSO<sub>4</sub>.

363

364

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373

### 374 **Supporting information**

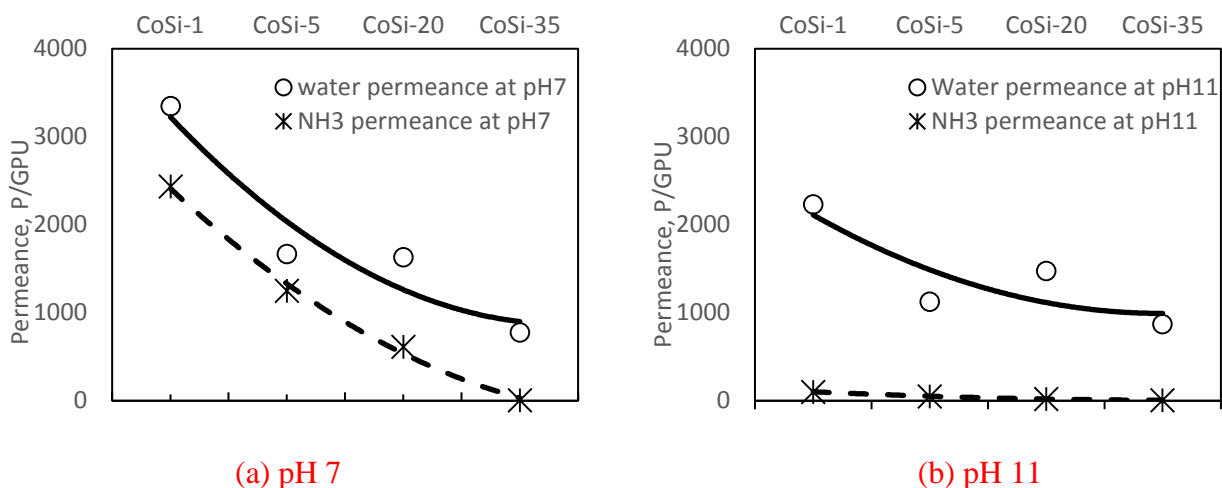
375

376 **Table A1 The respective partial pressure of ammonia and water based on distillation theory (pH 11**  
377 **and ammonia concentration of 280 mg-N/L)**

Temperature, ° C	Partial pressure of ammonia, Pa	Partial pressure of water, Pa	Separation factor for ammonia/water based on distillation theory
35	49.4	5607	27.7
40	61.4	7356	26.3
45	75.8	9556	25.0
50	93.0	12301	23.8
55	113.4	15696	22.7
60	137.4	19862	21.8
65	165.5	24935	20.9

378

379



380  
381 (a) pH 7 (b) pH 11  
382 Fig. A1 Permeances of water and ammonia of CoSi membranes at (a) pH 7 and (b) pH 11  
383  
384

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