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

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Abstract

This study demonstrated the application of a new type of interlayer-free cobalt-doped silica membrane in treating ammonia solutions by pervaporation applied towards wastewater treatment. For enhanced hydrothermal stability, cobalt-doped silica (CoSi) membranes with increasing cobalt concentrations from 1 to 35 mol% were prepared and evaluated, namely CoSi-1, 5, 20 and 35. These membranes exhibited high water fluxes of 66 $L \cdot m^{-2} \cdot h^{-1}$for CoSi-1 and 15.5 $L \cdot m^{-2} \cdot h^{-1}$for CoSi-35 at 45 °C. The fluxes of the membranes decreased with increasing cobalt concentration; while the rejection to total nitrogen (TN, ammonia nitrogen) increased and hence allowed selective passage of water molecules. Enhanced thermostability was observed for the membranes, particularly CoSi-35 that exhibited TN rejection up to 99% at high temperature of 65 °C and highly alkaline environment (pH>10). Also, the CoSi-35 membrane showed stable performance in treating ammonia present in industry wastewater by achieving stable TN and mineral rejections of 97% and 99%, respectively. Fouling was observed and confirmed by SEM morphological analysis and EDX elemental inspection. The results indicated the deposition of low solubility salts such as $CaSO_4$.

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

1. Introduction

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

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

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

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

2. Experimental

2.1 Membrane Materials and Characterisation

A series of CoSi membranes were prepared using a dual acid-base catalyzed sol gel and interlayer free approach reported by Elma et al.[21]. In this method, cobalt nitrate hexahydrate was used as a cobalt precursor, which was added into the silica sol after 3 hours of refluxing. The mixture was stirred for an additional 45 min to ensure homogeneity. The molar ratio of cobalt oxide in the silica sol was varied from 0 to 35 mol%, corresponding to pH range of 6 to 4.44 being above the isoelectric point (pH 1-3) of silica particles. The mixed sol was dried in an oven at 60 ºC for 24 hours to obtain dried gels , which was then grounded into powder and calcined at 600 ºC for 4 hours producing the CoSi gel. Hence, four membrane with different cobalt content of 1, 5, 20 and 35 mol% by dip-coating the gel four times onto the α-Al_2O_3 tubular substrate (Ceramic Oxide Fabricators, Australia) with macro-porous pore structure of 100 nm on average and outer diameter of 10 mm. The cross-section and surface of the virgin and used CoSi membranes were examined using a field emission scanning electron microscopy (FESEM). The surface chemistry and elemental information due to foulant deposition was quantified by a JEOL2100 microscope equipped with energy-dispersive x-ray spectroscope (EDS).

2.2 Membrane performance tests

Pervaporation experiments were performed using the setup described in previous work [10, 11], in which the membrane was submerged into a feed solution. The membrane tube, with an outer surface area of 17 cm^2, was blocked at one end and connected to vacuum line on the other end at an absolute pressure of 100–300 Pa. The feed solution was mixed homogeneously using a stirrer (stirring speed range: 300-1000 rpm) and heated to 35–65 ºC. Two liquid nitrogen cold traps were placed along the vacuum line to capture the vapour generated at 60 min intervals. During batch operation with small membrane area, the feed concentration was maintained constant by continuously supplying fresh feed. Tests under each condition were repeated three time (1-hour each) to ensure reproducibility. Both synthetic and industrial water samples were tested. After industrial sample testing, membrane cleaning was conducted with base and acid solutions separately, *i.e.*, 0.5% NaOH and 1 % HCl.

2.3 Test solutions

Synthetic feed solutions were prepared by adding 300 mg/L (equivalent to 280 mg-N/L) ammonia ammonium hydroxide (28-30% NH_3, Sigma-Aldrich) and 500 mg/L sodium chloride (NaCl) into deionized (DI) water, at both pH 7 and 11 adjusted by 2M HCl solution. Sodium chloride was added to maintain a realistic electrolytic balance in the solution for comparison with industry samples. A model industry wastewater (pH 7.5) was obtained from an ion exchange (IX) regeneration process from an industrial demineralisation plant. This sample was tested only at 45 ºC, which represents the readily available low-grade waste heat from industry [22].

2.4 Sample Analysis

The total nitrogen concentration (indicative of NH_3 concentration) of the feed and permeate samples was measured using the Total Nitrogen unit (Model no: TNM-1) of the Shimadzu TOC/TN analyser, followed the previous procedure reported in elsewhere [10]. All samples were analysed for elements (K, Mg, Na, Co, Si, P and S for sulphate) representing cations (anion for sulphate) by ICP-OES. Total dissolved solid (TDS) and solution pH were measured by a Hach portable meter with dual conductivity and pH probes. The composition of the fouling layer was examined through quantifying the elemental concentrations in the washed solutions.

2.5 Performance calculations

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

$$rejection = 1 - \frac{c_p}{c_f} \tag{1}$$

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

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

$$\alpha_{ij} = \frac{P_i^G}{P_j^G} = \frac{P_i^G/\ell}{P_j^G/\ell} \tag{2}$$

where P_i^G is the membrane gas permeability of component *i* (cm^3(STP)·cm/cm^{2}s·cmHg) and ℓ is the membrane thickness. P_i^G/ℓ is the permeance of component *i*. It can be defined as the component flux normalized for driving force across the membrane:

$$\frac{P_i^G}{\ell} = \frac{D_i \cdot K_i^G}{\ell} = \frac{j_i}{p_{io} - p_{i\ell}} \tag{3}$$

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

$$p_{io} = H_{io} x_{io}^L \tag{4}$$

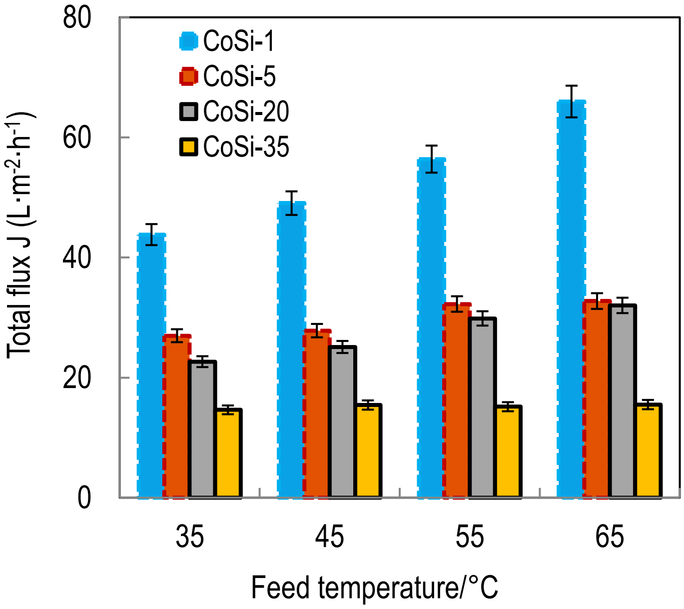
where H_{io} is the Henry's law constant [24] indicating the ammonia-ammonium equilibrium relationship, x_{io}^L is the mole fraction of the component *i* in the feed liquid. p_{il} is calculated based on the vacuum pressure of pervaporation and permeate concentration. The α_{ij} is indicative of the actual separation function of the membrane excluding the effect of process driving force and volatility difference, i.e., partial vapour pressure. An α_{ij} value of 1.0 will be expected if the membrane does not contribute to separation and is instead working completely by distillation, for which Table A1 is provided in the Supporting Information containing the respective partial pressure of water and ammonia in the temperature range of 35 to 65°C at pH 11. A value of below 1.0 indicates water selective feature of the membrane; otherwise ammonia selective when >1.0. In this paper, the symbol $\alpha_{NH3/H2O}$ is used for discussions.

3. Results and discussion

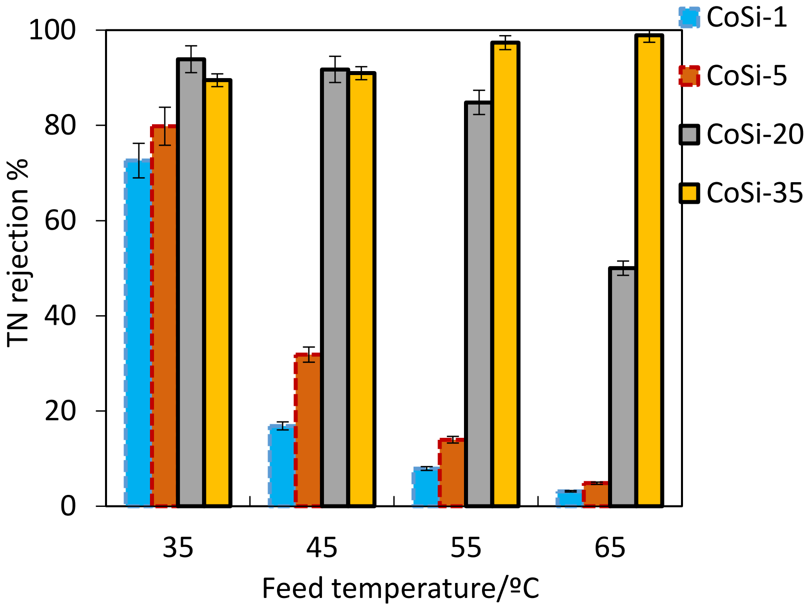
3.1 Separation performance of synthetic solutions

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

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



(a) Total flux



(b) TN rejection

Fig. 1 Total flux *J* and TN rejection rate of four cobalt doped interlayer free silica membranes with pH 7 synthetic ammonia solution in pervaporation (initial *TN*=280 mg-N/L, T_f=35-65ºC, Pv =100-300 Pa absolute, 3-hour PV test conducted under each condition)

The results in Fig. 1 confirms that the CoSi-35 membrane could be suitably applied to treat industry samples in similar pH conditions (6.0-8.0), however the proportion of free volatile ammonia is low, i.e. 2% at pH 7.0. So to better explore the ammonia rejecting property of the membranes, tests were conducted at higher pH of 11.0 as shown in Fig. 2, where more free volatile ammonia is present thus better confirming this effect of the silica material prior to testing on real industry samples. It was found that the membrane flux decreases with increasing cobalt concentration, except for CoSi-5 that showed a lower flux than that of CoSi-20. This may be related to its microporosity with low pore volume, as observed in a previous study [21]. Also, compared to the flux results at 65°C and pH 7 in Figure 1, it is observed that the flux for each CoSi membrane at pH 11 decreases or remains unchanged in Figure 2. This is because for these membranes, which exhibit water selectivity, the vapour flux is strongly affected by the fraction of free ammonia in the solution. Although ammonia has a relatively small chance of entering the membrane pores, it may still act to inhibit water flux at the pore surface. Similar to the observation from the pH 7.0 solution testing (Fig. 1), the TN rejection (in %) increases with increasing cobalt concentration, i.e., 4% and 87% for the CoSi-1 and CoSi-35 membranes, respectively. Given the larger fraction (99.8%) of free ammonia to total ammonia nitrogen in the pH 11.0 feed solution, the current results have shown consistent separation preference of the membrane towards water. Also, the stable performance of CoSi-35 has indicated the potential of cobalt surface modified silica membranes for treating wastewater containing ammonia nitrogen under alkaline and hydrothermal environment, which was challenging for silica membrane with γ-alumina interlayer [11].

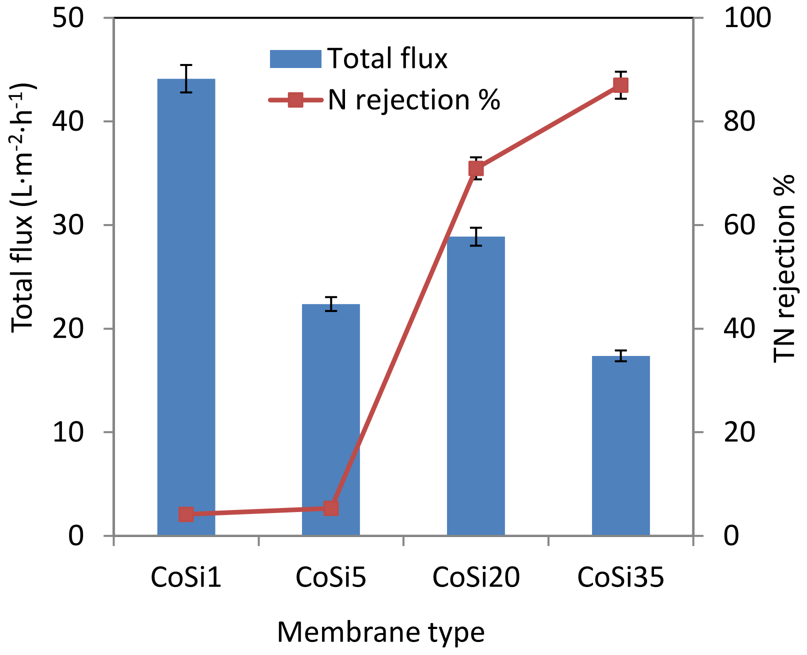


Fig. 2 Total flux *J* and TN rejection % of four Cobalt doped interlayer free silica membrane in synthetic ammonia solution with pH 11.0 (initial TN=280 mg/L, T_f=65ºC, Pv =100-300 Pa absolute, membrane area A=0.0017m^2)

The overall results of good TN rejection obtained by the cobalt-dope silica membranes, particularly CoSi-35, has indicated effective separation between ammonia and water. To reveal the intrinsic separation of the membranes, the molar permselectivity, $\alpha_{NH3/H2O}$ (Equation (2)), was calculated for the four CoSi membranes based on the performance at 65°C testing with pH 7.0 (Fig. 1) and pH 11.0 (Fig. 2) synthetic solutions. The $\alpha_{NH3/H2O}$ results are plotted in logarithmic scale, as shown in Fig. 3, with the *x*-axis starting from 1.0 where distillation separation effect for ammonia-water system is dominant. Two dashed lines for the respective pH conditions were set at α_{pH7}=0.76 and α_{pH11}=0.05 based on the permselectivity calculation where no separation occurs. It was found that the $\alpha_{NH3/H2O}$ values of all membranes at both pH values are below the respective benchmark lines, indicating truly water selective (or ammonia rejective) feature. Although high pH is favourable for the release of volatile ammonia (e.g., 99.8% of TN as free ammonia at pH 11.0 [12]) from its aqueous solution, the results of both pH have shown consistent separation behaviours of the CoSi membranes, particularly at high pH of 11 the $\alpha_{NH3/H2O}$ is much below 1.0. Also, the ammonia-water separation function is greatly enhanced with increasing cobalt concentration from 1 to 35 mol%, as indicated by the rapidly decreasing trend lines of the $\alpha_{NH3/H2O}$ at both pH conditions. The corresponding permeance data (Equation 3) of the membranes at both pH 7 and 11 is provided in the supporting materials as Fig. A1, where the respective permeance of water and ammonia show consistent trends of the separation mechanism of the CoSi membranes.

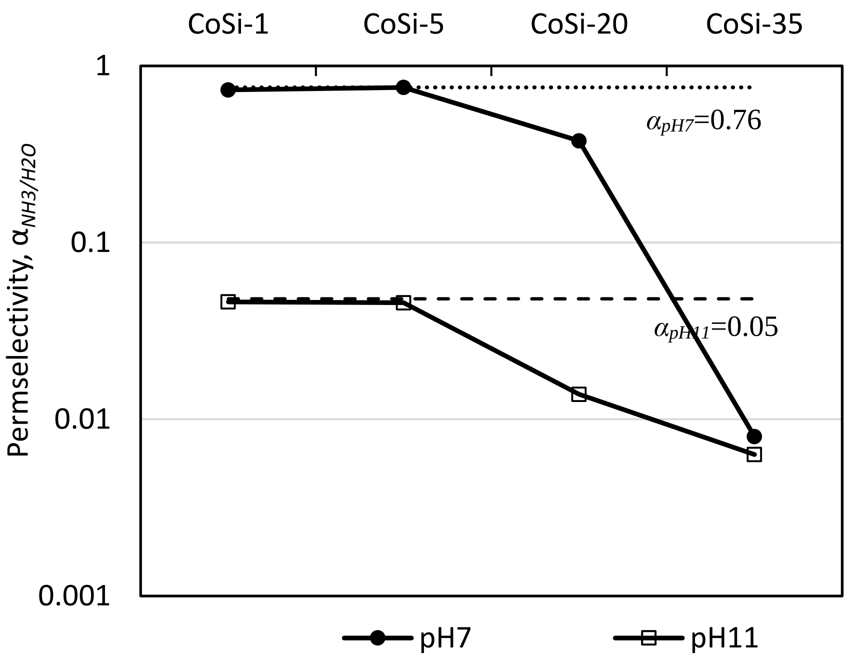


Fig. 3 Comparison of permselectivity $\alpha_{NH3/H2O}$ at various CoSi ratio (initial TN=280 mg/L, T_f=65ºC, pH=7.0&11.0, Pv =100-300 Pa absolute, membrane area A=0.0017m^2). Dashed lines indicate no separation (feed concentration = permeate concentration)

3.2 Membrane performance in industry wastewater testing

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

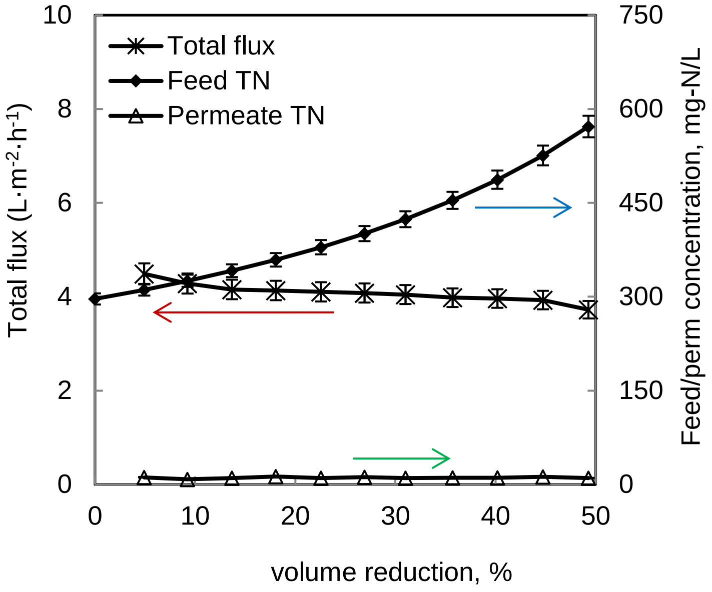


Fig. 4 Membrane performance of CoSi-35 using industry wastewater (initial ammonia concentration as 296 mg-N/L, pH=6.93, T_f=45°C, vacuum pressure =0.2±0.1 kPa absolute, stirring intensity 300rpm, membrane area A=0.0017m^2)

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

To reverse possible fouling, the membrane was cleaned with acid (0.5 wt%) and alkaline (1.0 wt%) solutions. Based on the flux data before and after cleaning in Table 2, the testing with pure water was used to benchmark of membrane performance and it shows that in the post-cleaning stage the flux was successfully restored to 73% of the original flux of the fresh membrane, indicating the partial removal of contaminants and effectiveness of membrane cleaning. Similarly, the subsequent test on the wastewater gave partially restored flux as 64% of the original value (4.7 L·m^{-2}·h^{-1}). Throughout the 60-hour testing, the membrane integrity was maintained exhibiting good hydrothermal stability of the membrane working under industrial water chemistry. The rejection of TN and other elements remained relatively stable throughout the operation, as shown in Table 1, in which the dissolved solids including Na, Ca, Mg, P and K salts were rejected more than 99% and the TN rejection was 97%. The rejection of total organic (TC) is lower than 50% due to the presence of inorganic carbon (as carbonic acid or bicarbonate) and low molecular weight organic carbon in the feed that easily pass through the membrane. Consistent with previous tests (Figs. 1 and 2), the presence of ammonia in the permeate is minimal. However, the presence of Ca^{2+} and SO_4^{2-} in the solution indicated the fouling potential, which is worth further investigation.

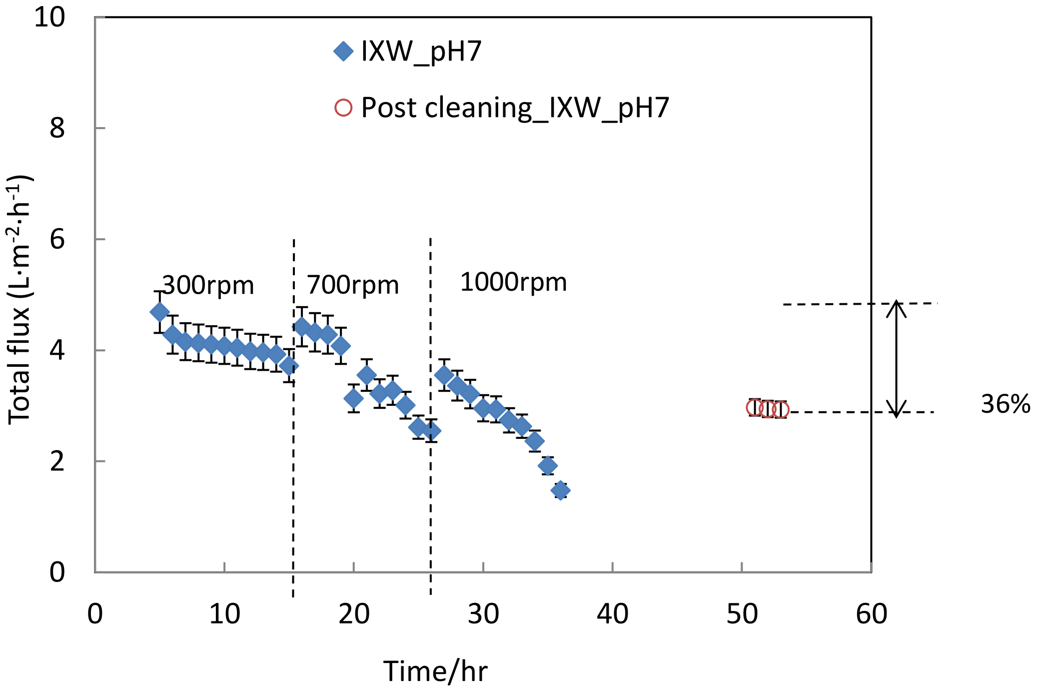


Fig.5 Membrane flux of CoSi-35 with industrial wastewater pH 7.4: (♦) new membrane ; (o) after chemical cleaning (initial TN=296 mg/L, T_f=45°C, vacuum pressure =100-300 kPa absolute, stirring speed: 300, 700 and 1000rpm, membrane area A=0.0017m^2)

Table 1 Rejection data of various species in industry wastewater sample testing throughout 60-hour 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
$\mathbf{K^+}$	3.7	<0.01	99.7
$\mathbf{Na^+}$	538	<0.1	99.9
P	3.36	<0.01	99.9
$\mathbf{Ca^{2+}}$	57.2	<0.01	99.9
$\mathbf{Mg^{2+}}$	6.9	<0.01	99.9
S	4.42	<0.01	99.9

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

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

Correspondingly, the elemental analysis of the cleaning solutions (acid and base) was measured by ICP-OES. The results are presentd in the bar chart in Fig. 6. It was found that the concentrations of the Ca are highest compared to other cations, indicating the precipitation of Ca salts on the membrane surface, which could be prevented through various approaches [25], e.g., by improving the flow dynamics to reduce surface polarization or using conventional pretreatment means such as anti-scalant or microfiltration membrane prior to the CoSi membranes for ammonia separation. The presence of SO_4^{2-} is indicated by the elmental analysis of S. Also, there was some amount of Si and Co (in minor concentrations of 0.03 and 0.009 mg/cm^2, respectively) present in the cleaning solutions. The Si could be related to its existence in the water sample (in 0.72 mg/L); while the Co could be due to slight dissolution from the membrane coating into the cleaning chemicals due to the use of basic solution that creates high pH evironment. This means that future cleaning strategies should be adjusted to avoid dissolution of both Si and Co.

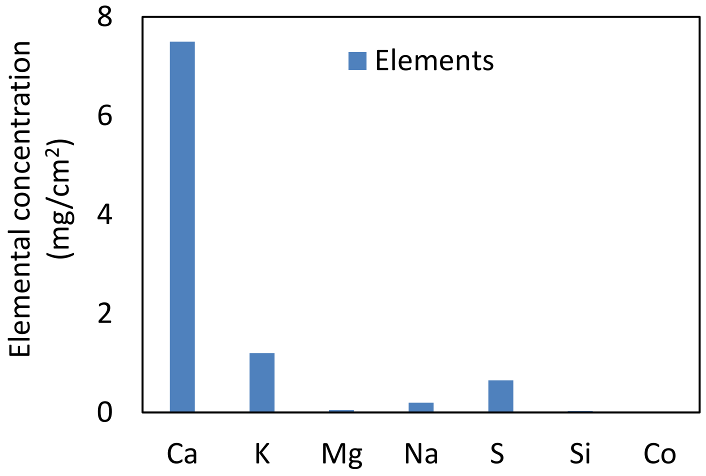


Fig. 6. Mineral content of cleaning solutions (acid and based added together) after 30h industry sample testing

According to the cross-section images of the CoSi membranes were shown in the previous work [21], where no distinct layers between the cobalt coating and the α–Al_2O_3 substrate, the infiltrated sol layer into the substrate is up to 10μm. This work only shows the SEM images of the surface morphologies of the untested (intact) and used CoSi-35 membrane after industry sample testing, as presented in Fig.

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

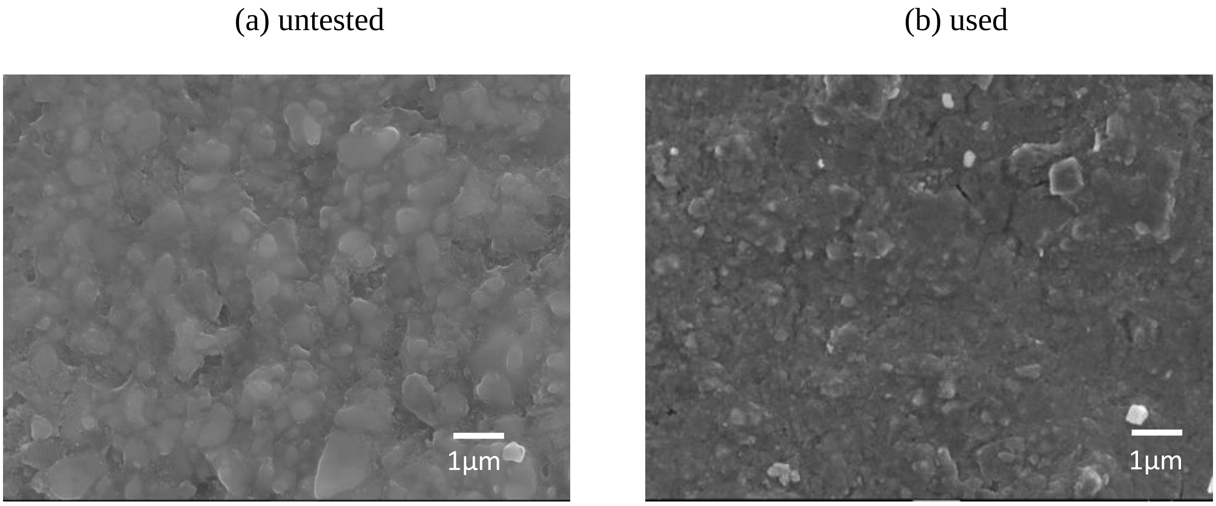


Fig. 7 SEM images of outer surface of CoSi-35 membrane before (untested) and after (used) pervaporation at 10,000x magnification with a scale bar of 1μm

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

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

Atom	**Energy**	**Atomic concentration (%)**	**Atomic concentration (%)**
	(keV)	**untested membrane**	**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
Total		**100**	**100**

4. Conclusions

This study has demonstrated the application of a new type of interlayer-free cobalt-doped silica membrane in treating ammonia containing wastewaters via pervaporation. The initial assessment using synthetic ammonium solutions showed that the interlayer-free membranes exhibited superior water flux and high rejection to ammonia, except for the membranes had low cobalt content such as CoSi-1 and CoSi-5 that failed at 65 °C and pH 11.0. Good hydrothermal stability of the cobalt-doped membranes was observed as the cobalt ratio increased in the cobalt silica coating. It was further demonstrated that the best performed CoSi-35 membrane was able to purify an industry wastewater, while the TN rejection remained high at 97% and rejection to minerals was above 99%. Although flux decline was detected over time, chemical cleaning was able to partially restore the membrane performance. Membrane autopsy results indicated the fouling propensity of the membrane that is susceptible to inorganic deposition particularly due to the presence of sparsely soluble salts such as $CaSO_4$.

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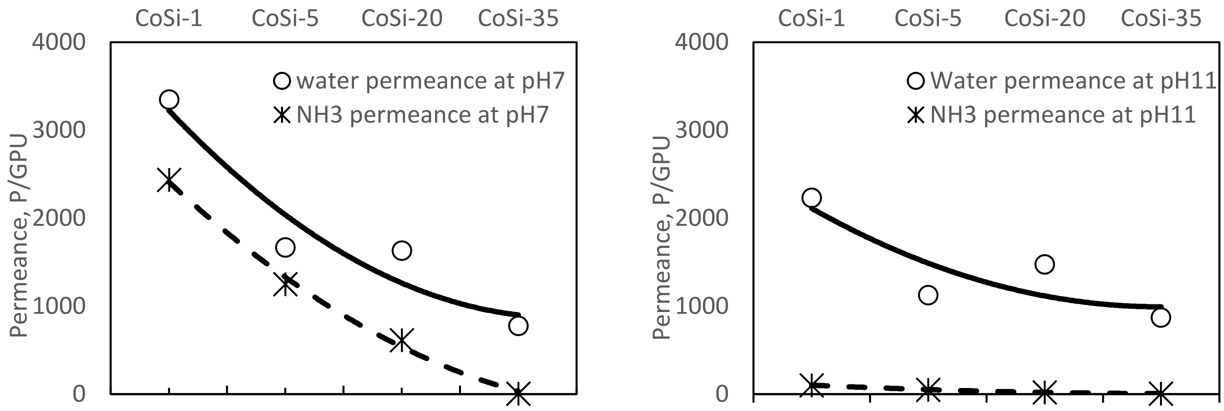
Supporting information

Table A1 The respective partial pressure of ammonia and water based on distillation theory (pH 11 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



(a) pH 7

(b) pH 11

Fig. A1 Permeances of water and ammonia of CoSi membranes at (a) pH 7 and (b) pH 11

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