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Chemistry and product quality of an NH_3–CO_2 forward osmosis desalination system

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ABSTRACT

This study examined the chemistry of a forward osmosis (FO) desalination system, which employs ammonium bicarbonate as the draw solute. The Indophenol blue photometric technique and a total carbon analyzer were used to determine the ammonia concentration and carbonate species concentration, respectively. The equilibrium relationships of the concerned species in water were used to analyze the distribution of ionic and gaseous species present in the solution at different stages of the process. The results can be used to evaluate the economic and environmental feasibility of the FO desalination process for water supply.

Keywords: Forward osmosis; Ammonia; Carbon dioxide; Draw solution; Concentration measurement; Drinking water

1. Introduction

Forward osmosis (FO) desalination has attracted considerable research interest because it has been suggested to have the potential to reduce the cost of seawater desalination compared to that of reverse osmosis (RO) [1]. In the FO process, the hydraulic pressure required for RO is replaced by the natural osmotic pressure gradient induced by the concentration difference between the feed and the draw solution. Therefore, the "draw solution" should have a higher osmotic pressure than the saline feed water to create the driving force for water to permeate through the membrane. The major expected advantages of the FO process include high feed water recovery, minimal brine discharge, and relatively low energy requirements and cost [2–5].

Although the idea of forward (or direct) osmosis desalination has a long history from 1960s [6,7], the technology has recently been revisited due to the growth of the desalination market, particularly because an aqueous solution of ammonia and carbon dioxide was proposed as its draw solution [1]. A previous study reported that the ammonia–carbon dioxide draw solution was highly competitive owing to its high osmotic pressure and readiness to dissolve into and separate from water [8].

Despite its thermodynamic advantages as a draw solute, the separation and recovery process of the ammonia–carbon dioxide solutions should be well

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designed to establish a commercially viable desalination process as it involves a complex chemical system. A 3 m^3/day FO desalination pilot has been constructed at the Korea Institute of Machinery and Materials for process development. The changes in the chemical composition in the process need to be measured or predicted clearly to control the product quality, as well as to understand the environmental impact that might be caused by the ammonia or carbonate species. In this study, analytic chemical techniques were used to evaluate the product quality and assess the separation and recovery performance in the FO desalination system.

2. Materials and methods

2.1. System description and pilot operation

Fig. 1 shows a schematic diagram of a FO desalination process. In a FO membrane module (A), water permeates from the feed, diluting the draw solution at the other side of the membrane. The product water is then separated from the solution in a separation column (B). The remainder of the solution is returned to the system to recover the initial concentration of the draw solution. The remaining gas that may exist and be emitted from the separation column of this pilot system is vented after scrubbing it with process water in a column (C) to maintain the system pressure.

In this study, the operation of only B and C columns shown in Fig. 2 was considered as this study focused on the removal and measurement of ammonia and carbon dioxide. To observe the separation and recovery performance, the effects of the membrane performance or module design have been set aside. The columns with a diameter of 0.2 m were filled with structured packing (AMT Pacific's SP-TYPE10) [9]. The packing height for the separation column was 3 m and that for recovery column was 1 m. The diluted solution of 2.3 L/min was heated to 100°C to produce 2 L/min of product water of the maximum quality.

The pilot was operated for three cases of diluted draw solutions at 0.5, 1.0, and 1.5 M. Samples of the product and waste water were taken to observe the change in their quality with the change in concentration of the draw solution.

The draw solution was prepared by dissolving ammonium bicarbonate in water. The ammonia and carbonate concentrations were measured using independent methods to examine the chemical compositions of the product, waste water, and other streams.

2.2. Ammonia determination

The total ammonia nitrogen (TAN) was determined using the Indophenol blue photometric technique [10]. The compositions of ammonia and the ammonium ion were then estimated from the equilibrium relation and pH of the sample solution.

An intensely blue compound, 4-(4-hydroxyphenyl) iminocyclohexa-2,5-dien-1-one (common name Indophenol), was formed by the reaction of ammonia, hypochlorite, and phenol catalyzed by sodium pentacyanonitrosylferrate(II) (common name sodium nitroprusside).

$$NH_3 + ClO^- + 2C_6H_5O^- \rightarrow O{=}C_6H_5{=}N - C_6H_4O^- + HO^- + 3Cl^- \tag{1}$$

The above reaction is based on the principle that the ammonium ion is released as ammonia gas upon the addition of sodium hydroxide (common name caustic soda).

$$NH_4^+ + OH^- \rightarrow NH_3(g) + H_2O \tag{2}$$

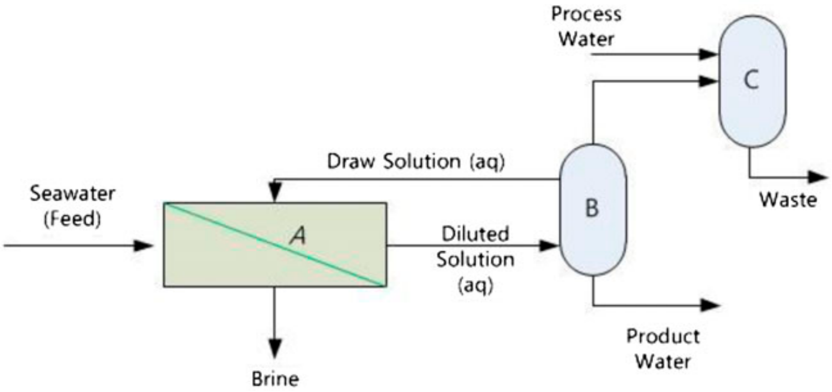

Fig. 1. Simplified schematic diagram of a forward osmosis desalination process. (A): forward osmosis membrane module; (B): separation and recovery column; (C): scrubbing column.

Fig. 2. Forward osmosis desalination pilot system at KIMM.

The reagents required for the Indophenol technique were prepared as follows:

(1) Sodium phenolate: 11.68 mL of phenol was mixed with 27.5 mL of sodium hydroxide, NaOH (20% w/v), and 3 mL of acetone. The solution was diluted to 100 mL.

(2) Sodium nitroprusside, IUPAC name sodium pentacyanonitrosylferrate(II): 0.15 g sodium nitroprusside was dissolved in 100 mL deionized water to produce a 0.15% w/v solution.

(3) Sodium hypochlorite: 21 mL of 10% (v/v) sodium hypochlorite was diluted up to 100 mL with deionized water to form a sodium hypochlorite solution.

(4) Standard ammonia solution: With the stock ammonia solution of a known concentration, standard solutions of 0.1, 0.3, 0.5, 0.7, and 1.0 (mg/L) are prepared to produce a calibration curve.

To prepare 34 mL of the sample, 10 mL of sodium phenolate, 1 mL of sodium nitroprusside solution, and 5 mL of sodium hypochlorite solution were added step-by-step with thorough mixing after each addition. The samples were then covered and kept aside for one hour to allow the color to develop. The absorbance at 630 nm was then measured using a spectrophotometer. The unknown concentrations were deduced from the calibration curve formed over the readings from the standard solutions.

The amount of ammonia was then estimated from the equilibrium relation between the ammonia and the ammonium ion in aqueous solution [11]. The TAN of the pilot system can be expressed as the summation of ammonia nitrogen and ammonium ion nitrogen.

$$\mathrm{TAN} = [\mathrm{NH_3 - N}] + [\mathrm{NH_4^+ - N}] \tag{3}$$

Therefore, the fraction of free ammonia can be expressed as follows [12]:

$$f = \frac{[\mathrm{NH_3 - N}]}{\mathrm{TAN}} \tag{4}$$

Note that the draw solution is assumed to be an aqueous solution without other ions. This includes, however, ionic carbonate species that would increase the fraction of the ammonium ion to some extent [12]. Therefore, the fraction of ammonia may be overestimated from this calculation.

For an aqueous solution at pH 6–10, at 0–50°C, the fraction of ammonia is [10]:

$$f = \frac{1}{(10^{(\mathrm{pK}_a - \mathrm{pH})} + 1)} \tag{5}$$

$$\mathrm{pK}_a = 0.0901821 + 2729.92/T_k \tag{6}$$

T is temperature in Kelvin.

The concentration of the ammonium ion was also measured by ion chromatography to confirm the results from the above estimation. During ion chromatography measurement, a sample is injected into a carrier solvent of pH 7, and it is not clear how much pH of the sample would be changed before the detection of ammonium ion. Reminding that the equilibrium between dissolved ammonia and ammonium ion is highly dependent on the pH of the solution, ion chromatography may not present a correct concentration. Meanwhile, Indophenol blue photometric technique measures the TAN, which is not affected by the pH of the solution. Although it also has a drawback: the detection range of ammonia concentration is very low with this method. The sample had to be diluted about 100 times to see the result, which means there should be a dilution error.

2.3. Carbonate determination

The total carbon concentration was determined using a total carbon analyzer, TOC-VCPH/CPN manufactured by Shimadzu Corporation. The inorganic carbon (IC), which was measured by total carbon (TC) analysis, consists of the carbon contained in carbonate, bicarbonate, and carbon dioxide dissolved in water. All carbonates are converted to carbon dioxide by acidifying the sample with a small amount of hydrochloric acid to obtain a pH of less than 3. This carbon dioxide is then volatilized by bubbling air or nitrogen through the sample.

A TOC-V IC reactor kit was used to sparge the IC reaction solution (acidified reaction liquid) with carrier gas. The sample was injected into the IC reaction vessel and the IC in the sample was converted to carbon dioxide, which was volatilized by the sparging process and detected by a NDIR (non Dispersive Infrared gas analyzer).

The results obtained were in the form of total inorganic carbon (TIC). The composition of the ionic ($\mathrm{HCO_3^-}$, $\mathrm{CO_3^{2-}}$) and gaseous ($\mathrm{H_2CO_3^*}$) species within the system can be obtained from equilibrium of carbonate species in water [13–15].

For dissolved carbon dioxide in water,

$$\mathrm{CO_2 + H_2O \leftrightarrow H_2CO_3^*} \tag{7}$$

where the dissociation constant, $\mathrm{pK_H} = 1.5$ at 25°C.

The first deprotonation stage,

$$\mathrm{H_2CO_3^* \leftrightarrow HCO_3^- + H^+} \tag{8}$$

where dissociation constant, $\mathrm{pK_1} = 6.3$ at 25°C.

At the second deprotonation stage,

$$\mathrm{H_2CO_3^- \leftrightarrow CO_3^{2-} + H^+} \tag{9}$$

where the dissociation constant, $\mathrm{pK_2} = 10.3$ at 25°C.

Assuming the system to be a closed one, the concentration of total carbonates species in solution, C_T, can be expressed as follows:

$$C_T = [\mathrm{H_2CO_3^*}] + [\mathrm{CO_3^{2-}}] + [\mathrm{HCO_3^-}] \tag{10}$$

The concentration of carbonate species, $\mathrm{H_2CO_3^*}$, $\mathrm{HCO_3^-}$, and $\mathrm{CO_3^{2-}}$, for a given C_T and pH can be determined using the following Eqs. (11–13):

$$\frac{[H_2CO_3^*]}{C_T} = \frac{1}{\left(1 + \frac{K_1}{[H^+]} + \frac{K_1K_2}{[H^+]^2}\right)} \quad (11)$$

$$\frac{[H_2CO_3^-]}{C_T} = \frac{1}{\left(1 + \frac{[H^+]}{K_1} + 1 + \frac{K_2}{[H^+]}\right)} \quad (12)$$

$$\frac{[CO_3^{2-}]}{C_T} = \frac{1}{\left(\frac{[H^+]^2}{K_1K_2} + \frac{[H^+]}{K_2} + 1\right)} \quad (13)$$

2.4. Product quality

The quality of the fresh water product from a desalination process should be controlled in light of water regulations. The entities of concern in the FO desalination system are as follows:

2.4.1. Ammonia

Ammonia is the measure of the most reduced inorganic form of nitrogen in water. Surface water can contain up to 12 mg/L [16]. The estimated daily ammonia intake through food and drinking water is 18 mg. In contrast, 4,000 mg of ammonia per day are produced endogenously in the human intestines. Ammonia has a toxic effect on healthy humans only if the intake becomes higher than the body's capacity to detoxify. Ammonia is not of direct importance for health at the concentrations expected in drinking water. Therefore, a health-based guideline has not been derived [16].

2.4.2. Total inorganic carbon

The TIC is the measure of the sum of carbonates, bicarbonates, and carbonic acid. The relative amount of each component is dependent on the pH of the water. At pH 7–8, which is typically encountered in most fresh water systems, the bicarbonate ion predominates (60–90% of the TIC). The bicarbonate concentrations in surface water are normally less than 500 mg/L and frequently less than 25 mg/L. No criteria have been set for the maximum permissible amount of TIC [17].

2.4.3. pH

According to the EPA, the noticeable effects of a $pH < 6.5$ include a bitter metallic taste and corrosion. The noticeable effects of pH above 8.5 include a slippery feel, soda-like taste and deposits [18].

2.4.4. Total dissolved solids

The total dissolved solids (TDS) are reported in mg/L with values in fresh water naturally ranging from 0 to 1,000 mg/L. High concentrations of TDS limit the suitability of water as a drinking source and irrigation supply. For industrial use, high TDS waters can interfere with the clarity, color, and taste of the manufactured products. The permissible limit for drinking water has been set to a maximum of 500 mg/L [18].

3. Results and discussion

The ammonia concentration in the product is of high interest in FO desalination systems based on ammonia and carbon dioxide. Table 1 lists the distribution of ammonia species in the standard draw solutions. At normal temperatures and pressures, the ammonia species are mainly in the ionic form.

Table 2 lists the ammonia concentrations in the products sampled from the pilot scale FO system. The results of the Indophenol blue photometric technique were compared with those from ion chromatography. The indophenol technique was expected to underestimate the amount of the ammonium ion in the solution, as in Cases 1 and 2. In Case 3, however, the concentration of the ammonium ion measured by ion chromatography was lower than that estimated by the indophenol technique and equilibrium relation. This may be due to the change in the pH of the solution with time or during dilution. Carbon dioxide might have dissolved into solution resulting in a decrease in pH, to which the ammonium ion concentration is closely related (see Eq. (5)). Table 3 depicts the concentra-

Table 1
Distribution of ammonia and ammonium ion in the standard draw solutions

Concentration (mol/L)	pH	Total ammonia nitrogen (ppm)	Ammonia, NH_3 (ppm)	Ammonium ion, NH_4^+ (ppm)
1.75	8.1	23,883	2,137	21,746
1.5	8.09	16,494	1,445	15,049
1	8.12	13,490	1,260	12,230
0.5	8.2	6,031	667	5,364
0.1	8.21	1,225	138	1,087
0.05	8.19	500	54	446

Table 2
Distribution of ammonia and ammonium ion in the product of the pilot scale FO desalination plant

Case	pH	Total ammonia nitrogen[a] (ppm)	Ammonia[b], NH_3 (ppm)	Ammonium ion[b], NH_4^+ (ppm)	Ammonium ion[c], NH_4^+ (ppm)
1	7.93	12.96	0.63	12.33	17
2	7.32	14.50	0.17	14.33	16
3	7.47	46.29	0.89	45.39	29

[a] Measured by the Indophenol blue photometric technique.
[b] Estimated from the TAN.
[c] Measured by ion chromatography.

tion and distribution of ammonia species in the waste water sampled from the pilot scale FO system.

Tables 4 and 5 present the results obtained for the carbonate species distribution in the standard draw solution samples and those for the samples from the FO pilot, respectively. For a given pH range under normal temperatures, carbon mostly exists in the form of the bicarbonate ion. Dissolved carbon dioxide and carbonate ions were found in traces. The percentage of the dissolved carbon dioxide gas was found to be higher than that of the carbonate ion.

The measured entities of ammonia, TIC, pH, and TDS were compared with their general permissible range for drinking water (Table 6).

Based on the obtained measurement results, the removal efficiency of the ammonia and carbonate species can be calculated to assess the separation performance, as shown in Tables 7 and 8. The inlet stream to the separation column is the diluted draw solution, to which water is permeated from the feed in the FO membrane module. Therefore, the separation efficiency is the ratio of the amount removed to that in the diluted draw solution. The separation column showed an ammonia removal efficiency of 99.7% for 1.5 M diluted draw solution.

As can be discerned from the discrepancies in the removal efficiency for ammonia and carbonates, Table 9 shows that the ammonia nitrogen to carbon ratio slightly changes during separation. The ratio was higher in the product water, i.e. more ammonia remained in the product than carbon dioxide. This is because the solubility of ammonia in water is much higher than that of carbon dioxide at a given temperature and pressure. Therefore, the separation of carbonate species is more effective compared to that of ammonia species.

Table 3
Distribution of ammonia and ammonium ion in the wastewater of the pilot scale FO desalination plant

Case	pH	Total ammonia nitrogen[a] (ppm)	Ammonia[b], NH_3 (ppm)	Ammonium ion[b], NH_4^+ (ppm)
1	7.09	0.63	0.005	0.62
2	6.98	17.13	0.10	17.02
3	5.97	68.05	0.04	68.01

[a] Measured by the Indophenol blue photometric technique.
[b] Estimated from the TAN.

Table 4
Distribution of carbonate species in the laboratory prepared standard draw solutions

Concentration (mol/L)	pH	Determined inorganic carbon (ppm)	Dissolved carbon dioxide $[H_2CO_3^*]$ (ppm)	Bicarbonate ion $[HCO_3^-]$ (ppm)	Carbonate ion $[CO_3^{2-}]$ (ppm)
1.75	8.1	1930	1546.95	96031.2	596
1.5	8.09	16,260	1332.64	80845.3	490.35
1.0	8.12	11,960	915.38	59502.9	386.7
0.5	8.2	5,701	363.4	28397.02	221.85
0.1	8.21	1,304	81.22	6495.94	51.95
0.05	8.19	624	40.71	3107.84	23.7

Table 5
Distribution of carbonate species in product and wastewater of the pilot scale FO desalination plant

Case	Total inorganic carbon (ppm)	Dissolved carbon dioxide $[H_2CO_3^*]$ (ppm)	Bicarbonate ion HCO_3^- (ppm)	Carbonate ion CO_3^{2-} (ppm)
Product				
1	9.85	0.22	9.58	0.04
2	10.12	0.88	9.23	0.010
3	9.54	0.60	8.92	0.014
Wastewater				
1	9.91	1.38	8.52	0.006
2	23.80	4.11	19.68	0.011
3	92.86	63.26	29.59	0.004

Table 6
Measured entities and their permissible range in water for drinking purposes

Entity	Measured	Regulation
(1) Ammonia (NH_3)	0.17–0.89 ppm	No general criteria (Surface water contains around 12 ppm) [12]
(2) Total inorganic carbon (TIC)	9.54–10.12 ppm	No general criteria (Bicarbonate in surface water is usually less than 25–500 ppm) [13]
(3) pH	7.32–7.93	6.5–8.5 [14]
(4) Total dissolved solids (TDS)	58–82 ppm	Less than 500 ppm [14]

Table 7
Ammonia removal efficiency

Case	Total ammonia nitrogen in diluted draw solution (ppm)	Total ammonia nitrogen in product (ppm)	Percentage removal (%)
1	6,031	12.96	99.8
2	13,490	14.50	99.9
3	16,494	46.29	99.7

Table 8
Carbonate removal efficiency

Case	Total inorganic carbon in diluted draw solution (ppm)	Total inorganic carbon in product (ppm)	Percentage removal (%)
1	5,701	9.85	99.8
2	11,960	10.12	99.9
3	16,260	9.54	99.9

Table 9
Ammonia nitrogen to carbon ratio in the dilute draw solution and product

Case	Ammonia nitrogen to carbon ratio	
	Dilute draw solution	Product
1	1.06	1.32
2	1.13	1.43
3	1.01	4.85

4. Conclusions

The distribution of ammonia and carbonate species in the draw solution samples with different concentrations, and product water samples from a FO desalination pilot system were evaluated. The trace amounts of species present in the product were compared with their respective general permissible ranges for drinking water. From the comparison, the product water from the FO desalination system can be considered safe for drinking purposes. However, it should be noted that this study does not consider the possible salt diffusion from the feed through the membrane. The salt rejection rates of the recently developed membranes are very close to 100%, but the product still may contain a little amount of feed salts. The remaining salts should be removed in a post-treatment process when necessary.

The removal efficiency of the separation system was measured by calculating the percentage change in the total dissolved species in terms of the TAN and total inorganic carbonate. The removal efficiency was found to be more than 99%, showing that almost all the dissolved draw solute had been removed in the FO desalination system to produce fresh water.

The results will contribute to assessing the environmental impact of the FO process for varied applications and economic analysis of the product water. The economic competence of the FO desalination system in comparison to the conventional and other innovative technologies can also be evaluated with further information on energy requirement of the system, which will be presented in our future work.

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References

[1] J.R. McCutcheon, R.L. McGinnis, M. Elimelech, A novel ammonia–carbon dioxide forward (direct) osmosis desalination process, Desalination 174 (2005) 1–11.

[2] R.L. Mcginnis, M. Elimelech, Energy requirements of ammonia–carbon dioxide forward osmosis desalination, Desalination 207 (2007) 370–382.

[3] J.R. McCutcheon, R.L. McGinnis, M. Elimelech, Desalination by ammonia–carbon dioxide forward osmosis: Influence of draw and feed solution concentrations on process performance, J. Membr. Sci. 278 (2006) 114–123.

[4] R.L. Mcginnis, M. Elimelech, Global challenges in energy and water supply: The promise of engineered osmosis, Environmental Science & Technology 42 (2008) 8625–8629.

[5] R. Semiat, Energy issues in desalination processes, Environ. Sci. Technol. 42 (2008) 8193–8201.

[6] B.W. Murray, Desalting seawater with ammonia, Part 2: Osmosis, Water and Sewage Works 115 (1968) 525.

[7] J.O. Kessler, C.D. Moody, Drinking water from seawater by forward osmosis, Desalination 18 (1976) 297–306.

[8] T. Kim, Y. Kim, C. Yun, H. Jang, W. Kim, S. Park, Systematic approach for draw solute selection and optimal system design for forward osmosis desalination, Desalination 284 (2012) 253–260.

[9] http://www.amtpacific.com/.

[10] A. Aminot, D.S. Kirkwood, R. Kérouel, Determination of ammonia in seawater by the indophenol-blue method: Evaluation of the ICES NUTS I/C 5 questionnaire, Mar. Chem. 56 (1997) 59–75.

[11] Ammonia (NH_3), Ammonium Ion (NH_4^+). Available from: http://www.isws.illinois.edu/nitro/terms.asp?lpg=sitemap&term=NH4.

[12] Calculation of Un-ionized Ammonia in Fresh Water, Storet Parameter Code 00619, Florida Department of Environmental Protection, Chemistry laboratory methods manual, Tallahassee, FL, Revision 2, December 02 2001.

[13] S. Emerson, J.I. Hedges, Chemical Oceanography and the Marine Carbon Cycle. Cambridge University Press, New York, NY, 2008, pp. 101–130.

[14] L.S. Vernon; J. DavidAcid-base chemistry, in: L.S. Vernon, J. David (Eds.), Water Chemistry, Wiley, New York, NY, 1980, pp. 156–172.

[15] The Chemistry of Ocean pH. Available from: http://joannenova.com.au/2011/11/the-chemistry-of-ocean-ph-and-acidification/.

[16] Ammonia in Drinking Water: Background Document for Development of WHO Guidelines for Drinking-water Quality, Originally published in Guidelines for drinking-water quality, 2nd ed., vol. 2, Health criteria and other supporting information, World Health Organization, Geneva, 1996.

[17] Interpreting Data. Available from: http://www.ilmb.gov.bc.ca/risc/pubs/aquatic/interp/interp-01.htm.

[18] Drinking Water Contaminants. Available from: http://water.epa.gov/drink/contaminants/index.cfm.