

정삼투 공정의 유도용질로서의 식물 회화학물질 기반의 탄닌산 유도체

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Phytochemical-based Tannic Acid Derivatives as Draw Solutes for Forward Osmosis Process

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요 약: 우리는 정삼투 공정의 유도용질로서 잠재적인 활용 가능성을 확인하기 위해 식물화학물질인 tannic acid (TA)에 알칼리 염 처리한 alkali tannate 염 중 하나인 potassium tannate (TA-K)를 평가하였다. TA-K의 정삼투 특성과 회수 특성은 체계적으로 조사되었다. 정삼투 공정을 active layer facing feed solution (AL-FS) 방식으로 적용했을 때, TA-K 유도용액의 투수량은 TA 유도용액의 투수량 보다 훨씬 많은 반면, TA 유도용액의 투수량이 거의 확인되지 않았다. 100 mM 저농도에서의 TA-K 유도용액의 삼투압(1,135 mOsmol/kg)은 NaCl 수용액의 삼투압(173 mOsmol/kg)의 약 6.5배로 확인되었다. 100 mM 농도의 TA-K의 투수량과 specific salt flux (6.14 LMH, 1.26 g/L)는 동일한 농도의 NaCl 유도용액의 투수량과 specific salt flux (2.46 LMH, 2.63 g/L)의 약 2.5배 및 0.5배로 각각 확인되었다. TA-K를 재사용하기 위해, 금속 이온 침전법을 이용하여 TA-K 유도용질을 침전시킨 후, membrane filtration을 이용하여 유도용질을 회수하였다. 이 연구는 식물화학물질을 정삼투 공정의 유도용질로서의 적용 가능성을 보여준다.

Abstract: Potassium tannate (TA-K), which is prepared by base treatment of the bio-renewable tannic acid (TA), was evaluated for its potential application as a draw solute for water purification by forward osmosis. The forward osmosis and recovery properties of TA-K were systematically investigated. In the application of forward osmosis through the active layer facing feed solution (AL-FS) method, the water flux of TA-K draw solution was significantly higher than that of the TA draw solution, while that of the latter was not identified. At a low concentration of 100 mM, the osmotic pressure (1,135 mOsmol/kg) of the TA-K draw solution was approximately 6.5 times that (173 mOsmol/kg) of the NaCl draw solution. Furthermore, the water flux and specific salt flux (6.14 LMH, 1.26 g/L) of the TA-K draw solution at 100 mM were approximately 2.5 and 0.5 times those of the NaCl draw solution (2.46 LMH, 2.63 g/L) at the same concentration, respectively. For reuse, TA-K was precipitated by using a metal ion and recovered through membrane filtration. This study demonstrates the applicability of a phytochemical material as a draw solute for forward osmosis.

Keywords: draw solute, forward osmosis, tannic acid, recovery

1. Introduction

Water shortage is one of the most serious problems in the Contemporary Age, and ensuring clean water supply to the society is a crucial need. Typical separation processes for obtaining clean water include reverse osmosis and forward osmosis. Reverse osmosis in-

volves application of high pressure to the feed solution to obtain pure water, forward osmosis method is based on the natural phenomenon induced by the osmotic gradient between the feed solution and the draw solution[1]. Consequently, forward osmosis technology has higher energy efficiency than reverse osmosis technology and is gaining attention as a next-generation

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desalination technology[2,3]. Forward osmosis includes a membrane filtration process and a recovery process for separating the draw solute from the permeate solution. For commercialization, it is important to reduce the energy required for the recovery process[4,5], and thus, various strategies have been adopted to reduce energy requirements and cost. Draw solute recovery methods can be categorized as direct usage, thermal treatment, stimulus-triggered separation, membrane filtration, and hybrid methods. In the direct use method, the draw solution is directly applied to forward osmosis to obtain drinking water without involving any recovery stage or used for agriculture. Sugars such as glucose and fructose, or inorganic salts (e.g. KCl, NaNO₃, (NH₄)₂HPO₄, *etc.*), which are used as draw solutes for forward osmosis, can be used directly in drinking water or for fertilizer[6-9]. The draw solutes employed in the thermal treatment method include NH₃-CO₂ and SO₂[10,11]. As reported by Elimelech *et al.*, NH₃-CO₂ is dissolved in water to obtain NH₄HCO₃ and induce osmosis; the draw solute is recovered by heating it above a certain temperature so that it decomposed into CO₂ and NH₃. While this process is advantageous in that it induces high osmotic pressure and allows for easy recovery of the draw solute, the water quality is poor because of the small amount of residual draw solute in fresh water[12]. Stimulus-triggered separation can be classified based on physical or chemical stimulus, and physical stimulus-triggered separations are further classified into thermal and magnetic separations. In the thermal method, the draw solute is separated from water by reversible phase transition of the draw solution after a certain critical temperature (lower critical solution temperature (LCST) and upper critical solution temperature (UCST) and has the advantage of a simple recovery process[13]. Active studies have been conducted on the draw solutes in the thermal separation[14-18]. Wang *et al.* used poly(*N*-isopropylacrylamide) (PNIPAm), which is a typical polymer with LCST characteristics, in the forward osmosis process[19]. Surface-modified magnetic nanoparticles (MNPs) containing hydrophilic molecules

such as 2-pyrrolidone, triethylene glycol, and hydrophilic polymers, e.g. poly(acrylic acid), dextran, poly(ethyleneglycol)diacid, and poly(sodium acrylate), which induce osmosis on the surface of MNPs, can be easily separated from water by magnetic separation[20-23].

Chemical stimulus-triggered separation is more advantageous in that water is separated from the draw solute via reactions that occur when chemicals are added or removed, without external energy. Chemical stimulus-triggered separation is based on pH, salt, and gas response. Draw solutes using the pH-responsive method utilize an organometallic salt, and the draw solute is recovered by adjusting its water solubility through pH modulation[24]. The salt-responsive method involves solidification and recovery of the draw solute (aluminum sulfate) by using a specific salt as the precipitant. Aluminum sulfate is recovered after the precipitation into aluminum hydroxide and calcium sulfate by the addition of calcium hydroxide as the precipitant[25]. The gas-responsive method uses a switchable polarity solvent (SPS) as a draw solute, which induces osmosis via the formation of ammonium and hydrogen carbonate salts with relatively high polarity from the reaction between amine and carbon dioxide with relatively low polarity, and water. The draw solute is recovered by phase separation from water when CO₂ is removed from the draw solution[26]. The draw solute can also be recovered through membrane filtration from the draw solution in which the phase transition occurred. Poly(sodium acrylate), poly(sodium 4-styrenesulfonate), and dendrimers draw solutes can be recovered through ultrafiltration (UF)[27-29], while divalent inorganic salts such as MgSO₄ and MgCl₂ can be recovered through nanofiltration (NF) and further recovered through reverse osmosis (RO)[30]. Complex draw solutes such as carboxylic acid-metal complexes (oxalic acid-metal complex and ethylenediaminetetraacetic acid-metal complex) can also be recovered by NF[31,32]. Finally, the hybrid system combines independent methods to recover draw solutes. For example, purified water can be obtained by treating with an

ionic liquid such as 2-methylimidazoles through forward osmosis-membrane distillation (FO-MD) as well as nanocomposite polymer hydrogel from magnetic heating[33,34].

Tannin, which is a polyphenol, is abundant in wood and is used in the medicine, dye, food, and rubber industries[35,36]. Depending on their structural characteristics, tannins are classified as gallotannins, ellagitannins, complex tannins, and condensed tannins, among which gallotannins and ellagitannins are hydrolysable tannins[37]. Tannic acid, a gallotannin, forms ester bonds between 6 to 9 gallic acid units and glucose, and is known to exhibit antioxidant, antibacterial, and anti-cancer activities, similar to other polyphenols[38-42]. The glucose core and branched gallic acid units have been reported as major contributors to the antioxidant properties of tannins[43]. Previous studies have reported that the trihydroxy group in the branched gallic acid unit plays an important role in determining the antioxidant properties of tannic acid, and hydrogen bonding between the trihydroxy groups in the molecule leads to the excellent antioxidant properties[43-45].

In this study, we developed a potassium tannate (TA-K) product, a phytochemical polyphenol, to identify the potential use of phytochemicals as draw solutes in forward osmosis, and investigated the forward osmosis and recovery characteristics of TA-K.

2. Experimental

2.1. Reagents and instrumentations

Tannic acid was purchased from Sigma Aldrich Co., LLC. Potassium hydroxide flake was purchased from Dae-Jung Chemical & Metals Co., LTD. Iron (III) chloride hexahydrate ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) and sodium chloride (NaCl) were purchased from Junsei Chemical Co., LTD., respectively. All reagents were used without further purification. To identify the molecular structure of the draw solute, we used Fourier-transform infrared (FT-IR) spectroscopy (Thermo Fisher Scientific, NICOLET 380) in the wavelength range from $4,000\text{ cm}^{-1}$ to 400 cm^{-1} with a resolution of 4 cm^{-1} in the attenuated total

reflection (ATR) mode. The thermal properties of the samples were analyzed by measuring weight changes with varying temperatures using a thermogravimetric analyzer (SETARAM Instrumentation, SETSYS Evolution). To identify and quantitatively analyze carbon, hydrogen, and oxygen atoms constituting the draw solute, we used an elemental analyzer (Elementar Analysensysteme GmbH, Vario Micro Cube). We also used an inductively coupled plasma atomic emission spectrophotometer (HORIBA JOBIN-YVON S.A.S., ACTIVA) to identify and quantitatively analyze the potassium atoms contained in the samples. The rheological properties of the samples were investigated by measuring the shear rate changes using a cone-and-plate rheometer with a diameter of 40 mm and a cone angle of 2° (TA Instrument, AR G2, stress control type). Conductivity was measured using a conductivity meter (METTLER TOLEDO, Seven2Go pro). The osmotic pressure was measured using an osmometer (KNAUER, SEMI-MICRO OSMOMETER K-7400) by the freezing point depression method. The water flux and reverse salt flux were determined by measuring the height difference between the solution levels on the two sides of a home-made U-shaped tube and the conductivity difference before and after the experiment, respectively.

2.2. Preparation of potassium tannate (TA-K)

The aqueous solution of potassium tannate, which is the draw solute used in the forward osmosis process, was prepared in 100 mL increments for each concentration using the following procedure. For example, a 100 mM aqueous solution of potassium tannate was prepared by adding 50 mL of potassium hydroxide (5 mol) aqueous solution was slowly added to 50 mL of tannic acid (200 mmol) aqueous solution at room temperature, followed by magnetic stirring. Potassium tannate aqueous solutions of other concentrations were prepared following the same procedure, with different amounts of tannic acid and potassium hydroxide. For example, 75 mM, 50 mM, and 25 mM aqueous solutions of potassium tannate were prepared by adding 150, 100 mmol, and 50 mmol of tannic acid and 3.75,

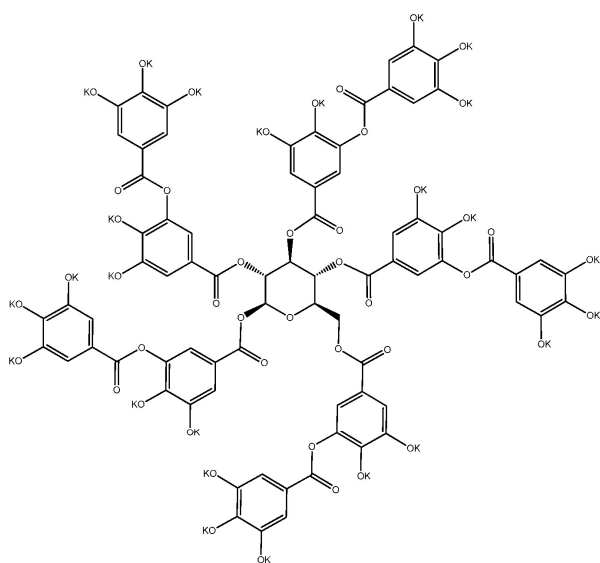


Fig. 1. Schematic structure of potassium tannate (TA-K).

2.5 mmol, and 1.25 mol of potassium hydroxide, respectively.

2.3. FO performance

The water flux and reverse salt flux were measured using a small-scale FO system connected to a home-made, cap-fixed L-shaped glass tube. The FO process was conducted after inserting the membrane (Hydration Technologies Inc. (HTI), thin film composite FO membrane) between two L-shape glass tubes with diameter of 2.3 cm and fixing with an aluminum clamp. The FO process was performed in the active-layer-facing feed solution (AL-FS) mode. Distilled water was added as feed solution to one side tube and NaCl, tannic acid, and potassium tannate solutions as draw solutions were added to the other side tube and the solutions were stirred at room temperature for 20 min using magnetic bar and solenoid (AS ONE, OCTOPUS CS-4).

The water flux (J_w) was determined by measuring the height difference between the solution levels on the two sides of the U-shaped tube and the reverse salt flux (J_s) was determined by analyzing the quantity of solute that diffused from the draw solution to the feed solution during the FO process; the total dissolved solid

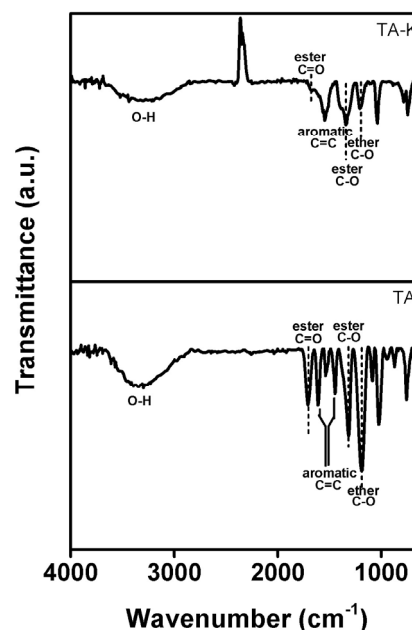


Fig. 2. FT-IR spectra of tannic acid (TA) and potassium tannate (TA-K).

(TDS) of the feed solution was also measured. The water flux (J_w , [$\text{Lm}^{-2}\text{h}^{-1}$, LMH]) and reverse salt flux (J_s , [$\text{gm}^{-2}\text{h}^{-1}$, gMH]) were calculated using Equation (1) and Equation (2), respectively.

$$J_w = \frac{\Delta V}{A \times \Delta t} \quad (1)$$

$$J_s = \frac{\Delta(C \times V)}{A \times \Delta t} \quad (2)$$

where Δt [h] is the operating time of the FO process; ΔV [L] is the volume change of the draw solution over time Δt ; A [m^2] is the effective membrane area, whose value is $4.15 \times 10^{-4} \text{ m}^2$; and ΔC [g/L] is the change in the concentration of the feed solution after time Δt .

3. Result and Discussion

3.1. Characterization of potassium tannate (TA-K)

Fig. 1 illustrates the molecular structure of TA-K. Tannic acid (TA) solution was treated with potassium

Table 1. Experimental and Theoretical Atomic Weight Percent of the TA and TA-K

	Atomic weight percent									
	Carbon (C) ^a		Hydrogen (H) ^a		Oxygen (O) ^a		Residue ^a	Potassium (K) ^b		
	Theo. value	Exp. value	Theo. value	Exp. value	Theo. value	Exp. value	Exp. value	Theo. value	Exp. value	
TA	53.64	47.90	3.06	3.60	43.30	48.50	— ^c	— ^d	— ^c	
TA-K	34.42	36.96	1.01	2.58	27.77	46.88	13.58	36.80	20.91	

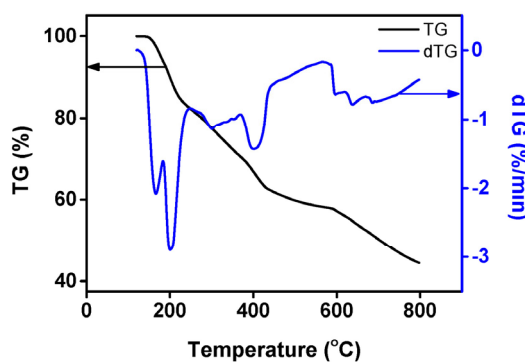
^aDetermined by elemental analyzer.

^bDetermined by inductively coupled plasma atomic emission spectrophotometer.

^cUnmeasured value experimentally.

^dUncalculated value due to absence of potassium atom structurally.

hydroxide (base) to prepare TA-K solution. FT-IR analysis was performed to identify the molecular structures of TA and TA-K (Fig. 2). The spectra of both TA and TA-K showed an O-H stretching vibrational peak in the range 3,550 cm^{-1} to 3,200 cm^{-1} ; a C=O stretching peak due to ester bonding at 1,740 cm^{-1} to 1,670 cm^{-1} ; aromatic C=C stretching at 1,600 cm^{-1} to 1,450 cm^{-1} ; C-O stretching of the ester at 1,370 cm^{-1} to 1,290 cm^{-1} ; and a C-O stretching peak of the ether at 1,210 cm^{-1} to 1,190 cm^{-1} . However, the intensity of the O-H peak of TA-K was lower than that of the O-H stretching vibrational peak of TA. The result suggests that the hydroxy group of TA was converted to hydroxide, and that TA-K was synthesized from TA. Another difference between the spectra was that the width of the aromatic C=C stretching peak of TA-K in the range 1,700 cm^{-1} to 1,500 cm^{-1} was larger than that in the TA spectrum, which is similar to the case of other tannate compounds, because TA-K is more strongly amorphous than TA[46]. Elemental analysis (EA) and inductively coupled plasma atomic emission spectrophotometry (ICP-AES) were performed to investigate the types and mass ratios of elements constituting TA and TA-K. Table 1 shows the theoretical and experimental values for the elements constituting each substance. Potassium was detected in the case TA-K but not TA, suggesting that the hydrogen moiety in the hydroxy group of the gallic acid units was converted to potassium. The hydrogen content measured by EA for TA-K (2.58 wt%) was higher than the theoretical value (1.01 wt%), and the potassium content measured

**Fig. 3.** Thermogravimetric curves of the potassium tannate (TA-K).

by ICP-AES (20.91 wt%) was lower than the theoretical value (36.80 wt%). In other words, the gallic acid units in TA were not completely converted to potassium gallate during the preparation of TA-K, and the conversion rate was approximately 57%.

3.2. Thermogravimetric analysis

Thermogravimetric analysis (TGA) was used to verify the thermal behavior of TA-K in the range 20°C to 800°C at the heating rate of 10 °C/min under argon atmosphere. The differential TG (dTG) curve, which shows the weight change over time, was also investigated (Fig. 3). According to the dTG curve, the thermal decomposition of TA-K proceeded in two steps. In the first step, decomposition started at approximately 130°C, and the decomposition rate was the maximum at approximately 250°C. A weight loss of approximately 18% occurred in the temperature range 130°C to 250°C. The thermal decomposition at approximately

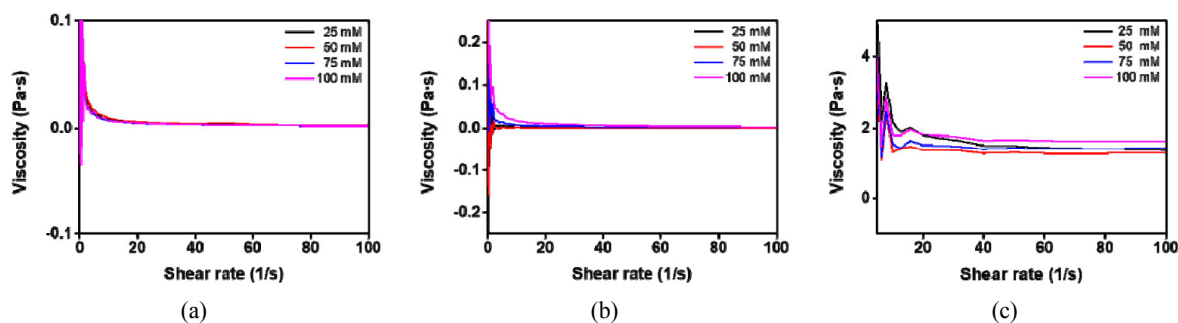


Fig. 4. Viscosity as a function of shear rate at room temperature: (a) NaCl, (b) TA, and (c) TA-K.

200°C was due to the partial breakdown of the intermolecular bonds of TA-K[47]. The rapid weight loss of 10% in the range 365°C to 450°C confirmed that the second thermal decomposition occurred at approximately 400°C, where the weight change was the maximum. This weight loss suggested that the ester bond between the gallic acid units of the tannate disintegrated due to the rupture of the intramolecular bonds[47,48]. The char yield at 800°C was approximately 44%, which corresponded to a mixture of potassium and carbon residue.

3.3. Viscosity

If the viscosity of the draw solute is high, the diffusion coefficient is low, resulting in slow molecular movement. This slow movement further leads to internal concentration polarization and external concentration polarization of the membrane, as well as a reduction in the water flux, suggesting that viscosity is an important factor affecting the efficiency of forward osmosis[4,49]. To evaluate the hydraulic properties of the TA-K draw solution, NaCl solution, a conventional draw solution, was used as a comparative group. Viscosity was measured at room temperature, and the shear rate was measured with changes from 0.1 s⁻¹ to 100 s⁻¹. Fig. 4 shows the viscosity graph based on the concentrations and shear rates of aqueous NaCl, TA, and TA-K solutions. According to Fig. 4(a) and 4(b), the viscosity of the NaCl solution at room temperature was approximately 0.0022 Pa·s to 0.0026 Pa·s, which did not show any large difference at the shear

rate of 100 s⁻¹ and in the range 25 mM to 100 mM. For the same shear rate and concentration range, the viscosity of the TA solution increased slightly 0.0014 Pa·s to 0.0029 Pa·s with increasing concentration, similar to the case of the NaCl solution. As shown in Fig. 4(c), the viscosity of the TA-K solution at the same shear rate and in the concentration range 25 mM to 100 mM was approximately 1.30-1.62 Pa·s, and only marginally higher than that of the NaCl and TA solutions in the entire measurement range; hence, TA-K shows high mobility, similar to a low-molecular-weight draw solute such as an inorganic salt, which suggests very small internal concentration polarization.

3.4. Conductivity

Conductivity is an indicator of the amount of draw solute ions present in the draw solution and is closely related to the degree of dissociation of the ion. Conductivity is closely related to the osmotic pressure, as will be described in the next paragraph[50], and higher conductivity typically leads to an increase in the osmotic pressure. The conductivity of the draw solution for different concentrations is shown in Fig. 5, and followed the order TA < NaCl < TA-K at the same concentration. The results suggest that the same concentration of TA-K will induce higher osmotic pressure than do the other two materials, and thus, TA-K exhibits better forward osmosis properties. Although the conductivity of the NaCl and TA-K solutions increased with increasing concentration, the

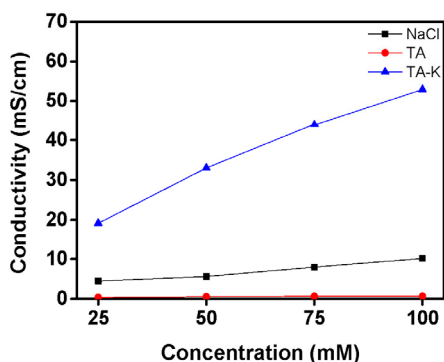


Fig. 5. Comparison of conductivity of NaCl, TA, and TA-K.

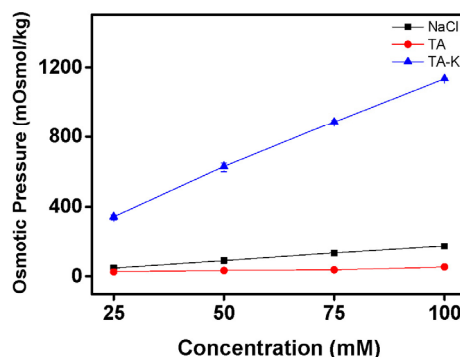


Fig. 6. Osmotic pressure according to the concentration of NaCl, TA, and TA-K.

change in the conductivity of the TA solution was smaller than that for the other two materials. This phenomenon was due to the difference in the nature (ionic and nonionic) of the materials. NaCl dissociates into Na^+ and Cl^- , and TA-K dissociates into potassium and tannate ions, while TA exists in a nonionic form at the given pH level. Other studies comparing the forward osmotic properties of ionic and nonionic materials showed similar results[19]. On the other hand, the conductivity of the TA-K solution was higher than that of the NaCl solution in the measured concentration range because of the greater number of dissociated ions from TA-K at the same molarity.

3.5. Osmotic pressure

The osmotic pressure of the draw solution is an important parameter determining the water flux in the forward osmosis process. The osmotic pressures of TA-K were measured for different concentrations, in addition to those for the aqueous NaCl and TA solutions. Fig. 6 plots the osmotic pressure for each draw solution as a function of concentration. The osmotic pressures of the draw solutions at all concentrations followed the order $\text{TA} < \text{NaCl} < \text{TA-K}$, and tended to increase linearly with increasing concentration. The changes in the osmotic pressure of the TA solution with increasing concentration were less notable than those for the other two solutions. The osmotic pressure of the TA-K solution was higher than that of the NaCl solution over the measured concentration

range, which can be explained by the Van't Hoff factor for colligative properties. TA-K is a combination of a tannate anion with a phenolate moiety and a potassium cation. Furthermore, the osmotic pressure of the TA-K solution was higher than that of the NaCl solution because of the greater number of TA-K ions at the same molarity. For example, at 100 mM, the osmotic pressure of the TA-K solution was 1,135 mOsmol/kg, which was approximately 6.5 times that of the NaCl solution (173 mOsmol/kg). These results suggest that the TA-K draw solution can exhibit a very high osmotic pressure of 1,000 mOsmol/kg or more, despite its low concentration of 0.1 M.

3.6. Water flux (J_w), reverse salt flux (J_s), and specific salt flux (J_s/J_w)

To optimize the forward osmosis process, it is important to consider the bidirectional diffusion of water and the draw solute[51]. Specific salt flux is a ratio of reverse salt flux to water flux, and is used as a loss index of the draw solute[52]. The higher the specific salt flux, the greater is the loss of draw solute, and thus, the lower is the process efficiency. To identify the applicability of TA-K as draw solute with a higher osmotic pressure than that of other two solutions, the water flux, reverse salt flux, and specific salt flux were determined for various concentrations of each draw solution. As shown in Fig. 7(a), the water flux of the draw solutions at the same concentration was in the or-

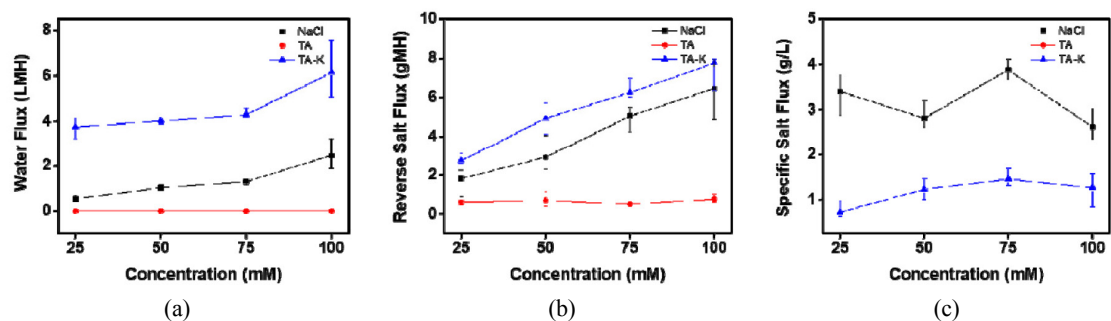


Fig. 7. Forward osmotic properties of each draw solutes: (a) water flux, (b) reverse salt flux, and (c) specific salt flux.

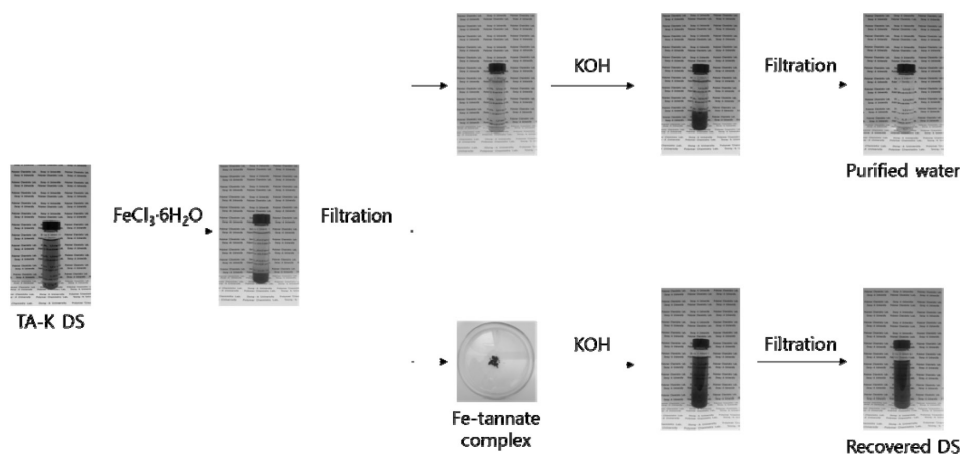


Fig. 8. Schematic recovery process of TA-K draw solution.

der $TA < NaCl < TA-K$, and it increased as the concentrations of the TA-K and NaCl solutions increased. This phenomenon occurs because the higher the concentration of the draw solution, the greater is the driving force of the osmotic pressure, and thus, the higher is the water flux permeating the membrane. Nevertheless, the water flux was nearly to 0 LMH even with increasing concentration of TA solution. As shown in Fig. 7(b), although the reverse diffusion of TA solution showed no significant difference with concentration, the reverse salt fluxes of the TA-K solution and NaCl solution increased with increasing concentration. The reverse salt flux of the TA-K solution was higher than that of the TA and NaCl solutions in the entire measured concentration range. This is because salt diffusion occurred due to the difference in concentration between the feed solution and the draw solution, and the number of ions in the TA-K draw solution at the

same concentration was more than that in the other two draw solutes. Fig. 7(c) shows the specific salt flux of each draw solution according to concentration. Unfortunately, since the water flux of TA was hardly measured, it was impossible to define a specific salt flux. The specific salt flux of the TA-K draw solution was lower than that of the NaCl draw solution at all concentrations. The result suggests that the efficiency of the forward osmosis process is higher when using TA-K as the draw solute than when using NaCl, and the replenishment cost of TA-K is lower than that of NaCl.

3.7. Recovery

For continuous use, the draw solute must be separated from water. For separation from the aqueous solution containing TA-K, the tannate was precipitated by complexation with metal ions and further recovered by

filtration[53-55]. Fig. 8 shows the recovery of TA-K for reuse after forward osmosis. The tannate was precipitated by complexation with Fe^{3+} ions via the addition of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ to the used TA-K draw solution, and the aqueous solution and Fe-tannate complex were obtained through filtration. Purified water was obtained by filtration of the solution, and KOH was added to precipitate the residual Fe^{3+} ions in solution after the complex was filtered off. After $\text{Fe}(\text{OH})_3$ was precipitated by adding KOH solution to the Fe-tannate complex, the precipitate was filtered to recover the draw solute.

4. Conclusion

In this study, we prepared and characterized potassium tannate (TA-K) as the draw solute of a forward osmosis process. The forward osmosis properties of the potassium tannate draw solution were superior to that of the conventional draw solute, i.e. NaCl. For example, at a concentration of 100 mM, the water flux (6.14 LMH) and the specific salt flux (1.26 g/L) of the TA-K draw solution were ~2.5 times the water flux (2.46 LMH) and ~0.5 times the specific salt flux (2.63 g/L) of the NaCl draw solution, respectively. The results confirmed that forward osmosis using TA-K as the draw solute is more efficient than that using NaCl. TA-K was recovered through a continuous process involving metal-ion precipitation and membrane filtration. TA-K, which is derived from plant-based and renewable resources, can be considered as a draw solute candidate in forward osmosis.

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Reference

1. N. Akther, A. Sodiq, A. Giwa, S. Daer, H. A. Arafat, and S. W. Hasan, "Recent advancements in forward osmosis desalination: A review", *Chem. Eng. J.*, **281**, 502 (2015).
2. M. Wilf, "Future of the osmotic processes", *Desalin. Water Treat.*, **15**, 292 (2010).
3. L. Chekli, S. Phuntsho, H. K. Shon, S. Vigneswaran, J. Kandasamy, and A. Chanan, "A review of draw solutes in forward osmosis process and their use in modern applications", *Desalin. Water Treat.*, **43**, 167 (2012).
4. Q. C. Ge, M. M. Ling, and T. S. Chung, "Draw solutions for forward osmosis processes: developments, challenges, and prospects for the future", *J. Membrane Sci.*, **442**, 225 (2013).
5. B.-M. Jun, S.-W. Han, Y.-K. Kim, N. T. P. Nga, H.-G. Park, and Y.-N. Kwon, "Conditions for ideal draw solutes and current research trends in the draw solutes for forward osmosis process", *Membr. J.*, **25**, 132 (2015).
6. T. Y. Cath, A. E. Childress, and M. Elimelech, "Forward osmosis: principles, applications, and recent developments", *J. Membr. Sci.*, **281**, 70 (2006).
7. R. E. Kravath and J. A. Davis, "Desalination of sea water by direct osmosis", *Desalination*, **16**, 151 (1975).
8. J. O. Kessler and C. D. Moody, "Drinking water from sea water by forward osmosis", *Desalination*, **18**, 297 (1976).
9. S. Phuntsho, H. K. Shon, S. Hong, S. Lee, and S. Vigneswaran, "A novel low energy fertilizer driven forward osmosis desalination for direct fertigation: Evaluating the performance of fertilizer draw solutions", *J. Membr. Sci.*, **375**, 172 (2011).
10. J. R. McCutcheon, R. L. McGinnis, and M. Elimelech, "A novel ammonia-carbon dioxide forward (direct) osmosis desalination process", *Desalination*, **174**, 1 (2005).

11. G. W. Batchelder, "Process for the demineralization of water", US Patent 3,171,799, March 2 (1965).
12. H. Luo, Q. Wang, T. C. Zhang, T. Tao, A. Zhou, L. Chen, and X. Bie, "A review on the recovery methods of draw solutes in forward osmosis", *J. Water Process Eng.*, **4**, 212 (2014).
13. Z. Wei, Q. Yu, and Z. Gan, "Thermosensitive block copolymers PEG-b-PBEMAGG containing functional pendant amino groups", *Macromol. Res.*, **20**, 313 (2012).
14. T. Maeda, Y. Akasaki, K. Yamamoto, and T. Aoyagi, "Stimuli-responsive coacervate induced in binary functionalized poly(*N*-isopropylacrylamide) aqueous system and novel method for preparing semi-IPN microgel using the coacervate", *Langmuir*, **25**, 9510 (2009).
15. K. Soppimath, T. Aminabhavi, A. Dave, S. Kumbar, and W. Rudzinski, "Stimulus-responsive "Smart" hydrogels as novel drug delivery systems", *Drug Dev. Ind. Pharm.*, **28**, 957 (2002).
16. J. Kim, H. Kang, Y.-S. Choi, Y. A. Yu, and J.-C. Lee, "Thermo-responsive oligomeric poly(tetrabutylphosphonium styrenesulfonate)s as draw solutes for forward osmosis (FO) applications", *Desalination*, **381**, 84 (2016).
17. Y. Zhong, X. Feng, W. Chen, X. Wang, K.-W. Huang, Y. Gnanou, and Z. Lai, "Using UCST ionic liquid as a draw solute in forward osmosis to treat high-salinity water", *Environ. Sci. Technol.*, **50**, 1039 (2016).
18. J. Kim, J. S. Chung, H. Kang, Y. A. Yu, W. J. Choi, H. J. Kim, and J.-C. Lee, "Thermo-responsive copolymers with ionic group as novel draw solutes for forward osmosis processes", *Macromol. Res.*, **22**, 963 (2014).
19. D. Li, X. Zhang, J. Yao, G. P. Simon, and H. Wang, "Stimuli-responsive polymer hydrogels as a new class of draw agent for forward osmosis desalination", *Chem. Commun.*, **47**, 1710 (2011).
20. H. W. Bai, Z. Y. Liu, and D. D. Sun, "Highly water soluble and recovered dextran coated Fe₃O₄ magnetic nanoparticles for brackish water desalination", *Sep. Purif. Technol.*, **81**, 392 (2011).
21. Q. C. Ge, J. C. Su, T.-S. Chung, and G. Amy, "Hydrophilic superparamagnetic nanoparticles: synthesis, characterization, and performance in forward osmosis processes", *Ind. Eng. Chem. Res.*, **50**, 382 (2011).
22. M. M. Ling, K. Y. Wang, and T.-S. Chung, "Highly water-soluble magnetic nanoparticles as novel draw solutes in forward osmosis for water reuse", *Ind. Eng. Chem. Res.*, **49**, 5869 (2010).
23. P. Dey and E. L. Izake, "Magnetic nanoparticles boosting the osmotic efficiency of a polymeric FO draw agent: Effect of polymer conformation", *Desalination*, **373**, 79 (2015).
24. W. T. Hough, "Forward-osmosis solvent extraction", US Patent 3,721,621, March 20 (1973).
25. B. S. Frank, "Desalination of sea water", US Patent 3,670,897, June 20 (1972).
26. M. L. Stone, C. Rae, F. F. Stewart, and A. D. Wilson, "Switchable polarity solvents as draw solutes for forward osmosis", *Desalination*, **312**, 124 (2013).
27. Q. Ge, J. Su, G. L. Amy, and T.-S. Chung, "Exploration of polyelectrolytes as draw solutes in forward osmosis processes", *Water Res.*, **46**, 1318 (2012).
28. E. Tian, C. Hu, Y. Qin, Y. Ren, X. Wang, X. Wang, P. Xiao, and X. Yang, "A study of poly(sodium 4-styrenesulfonate) as draw solute in forward osmosis", *Desalination*, **360**, 130 (2015).
29. S. Adham, J. Oppenheimer, L. Liu, and M. Kumar, "Dewatering reverse osmosis concentrate from water reuse applications using forward osmosis", Water Reuse Foundation, Alexandria (2007).
30. A. Achilli, T. Y. Cath, and A. E. Childress, "Selection of inorganic-based draw solutions for forward osmosis applications", *J. Membr. Sci.*, **364**, 233 (2010).
31. Q. Ge and T.-S. Chung, "Oxalic acid complexes: promising draw solutes for forward osmosis (FO) in protein enrichment", *Chem. Commun.*, **51**, 4854

- (2015).
32. Y. T. Zhao, Y. W. Ren, X. Z. Wang, P. Xiao, E. L. Tian, X. Wang, and J. Li, "An initial study of EDTA complex based draw solutes in forward osmosis process", *Desalination*, **378**, 28 (2016).
 33. A. Razmjou, M. R. Barati, G. P. Simon, K. Suzuki, and H. T. Wang, "Fast deswelling of nanocomposite polymer hydrogels via magnetic field-induced heating for emerging FO desalination", *Environ. Sci. Technol.*, **47**, 6297 (2013).
 34. S. K. Yen, M. Su, K. Y. Wang, and T.-S. Chung, "Study of draw solutes using 2-methylimidazole-based compounds in forward osmosis", *J. Membr. Sci.*, **364**, 242 (2010).
 35. M. N. Belgacem and A. Gandini, "Monomers, polymers and composites from renewable resources, Elsevier, Amsterdam (2011).
 36. K. Khanbabaee and T. van Ree, "Tannins: Classification and definition", *Nat. Prod. Rep.*, **18**, 641 (2001).
 37. V. L. Singleton, "Naturally occurring food toxicants: Phenolic substances of plant origin common in foods", *Adv. Food Res.*, **27**, 149 (1981).
 38. M. C. Figueroa-Espinoza, A. Zafimahova, P. G. M. Alvarado, E. Dubreucq, and C. Poncet-LeGrand, "Grape seed and apple tannins: Emulsifying and antioxidant properties", *Food Chem.*, **178**, 38 (2015).
 39. K.-T. Chung, S. E. Stevens Jr, W.-F. Lin, and C. I. Wei, "Growth inhibition of selected food-borne bacteria by tannic acid, propyl gallate and related compounds", *Lett. Appl. Microbiol.*, **17**, 29 (1993).
 40. K.-T. Chung, G. Zhao, E. Stevens Jr, B. A. Simco, and C. I. Wei, "Growth inhibition of selected aquatic bacteria by tannic acid and related compounds", *J. Aquat. Anim. Health*, **7**, 46 (1995).
 41. E. M. Daniel and G. D. Stoner, "The effects of ellagic acid and 13-*cis*-retinoic acid on *N*-nitrosobenzylmethylamine-induced esophageal tumorigenesis in rats", *Cancer Lett.*, **56**, 117 (1991).
 42. I. Gülçin, Z. Huyut, M. Elmastaş, and H. Y. Aboul-Enein, "Radical scavenging and antioxidant activity of tannic acid", *Arabian J. Chem.*, **3**, 43 (2010).
 43. C. A. Rice-Evans, N. J. Miller, and G. Paganga, "Structure-antioxidant activity relationships of flavonoids and phenolic acids", *Free Radical Biol. Med.*, **20**, 933 (1996).
 44. J. S. Wright, E. R. Johnson, and G. A. DiLabio, "Predicting the activity of phenolic antioxidants: Theoretical method, analysis of substituent effects, and application to major families of antioxidants", *J. Am. Chem. Soc.*, **123**, 1173 (2001).
 45. B. Badhani, N. Sharma, and R. Kakkar, "Gallic acid: A versatile antioxidant with promising therapeutic and industrial applications", *RSC Adv.*, **5**, 27540 (2015).
 46. J. Iglesias, E. G. De Saldaña, and J. Jaén, "On the tannic acid interaction with metallic iron", *Hyperfine Interact.*, **134**, 109 (2001).
 47. Z. Xia, A. Singh, W. Kiratitanavit, R. Mosurkal, J. Kumar, and R. Nagarajan, "Unraveling the mechanism of thermal and thermo-oxidative degradation of tannic acid", *Thermochim. Acta*, **605**, 77 (2015).
 48. M. Özacar, C. Soykan, and I. A. Şengil, "Studies on synthesis, characterization, and metal adsorption of mimosa and valonia tannin resins", *J. Appl. Polym. Sci.*, **102**, 786 (2006).
 49. Q. Ge, P. Wang, C. Wan, and T.-S. Chung, "Polyelectrolyte-promoted forward osmosis-membrane distillation (FO-MD) hybrid process for dye wastewater treatment", *Environ. Sci. Technol.*, **46**, 6236 (2012).
 50. W. D. Kemper and N. A. Evans, "Movement of water as effected by free energy and pressure gradients III. restriction of solutes by membranes", *Soil Sci. Soc. Am. J.*, **27**, 485 (1963).
 51. N. T. Hancock and T. Y. Cath, "Solute coupled diffusion in osmotically driven membrane processes", *Environ. Sci. Technol.*, **43**, 6769 (2009).
 52. W. A. Phillip, J. S. Yong, and M. Elimelech, "Reverse draw solute permeation in forward osmosis: modeling and experiments", *Environ. Sci.*

- Technol.*, **44**, 5170 (2010).
53. T. K. Ross and R. A. Francis, "The treatment of rusted steel with mimosa tannin", *Corros. Sci.*, **18**, 351 (1978).
54. F. Paiva-Martins and M. H. Gordon, "Interactions of ferric ions with olive oil phenolic compounds", *J. Agric. Food Chem.*, **53**, 2704 (2005).
55. P. Kraal, B. Jansen, K. G. J. Nierop, and J. M. Verstraten, "Copper complexation by tannic acid in aqueous solution", *Chemosphere*, **65**, 2193 (2006).