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Circulation of boron resources from desalination brine through solvent extraction (TMPD/2-ethylhexanol with kerosene) and ionic-liquid extraction (ALiCy/kerosene) methods

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Abstract−Desalination technologies have been widely implemented since the 1970s to solve the problem of freshwater scarcity. However, brine, the by-product of the desalination process, which has a higher salinity and total dissolved solids (TDS) than seawater, can cause severe environmental problems. For instance, brine could change the composition and temperature of seawater, decrease dissolved oxygen, and influence the organism's habitat. Under this circumstance, circulating critical resources from brine is acceptable for minimizing brine disposal. This study employed two extraction systems (TMPD, 2,2,4-trimethyl-1,3-pentanediol and ALiCy, trioctyl/decylmethylammonium-bis(2,4,4-trimethilpentyl) phosphinate), which are solvent extraction and ionic liquid extraction, to recover boron from brine. The parameters, including pH value, concentrations of TMPD and ALiCy, O/A (organic/aqueous) and I/A (ionic liquid/aqueous) ratios, contacting time, and reaction temperature of boron extraction through the TMPD and ALiCy systems, would be optimized. The results reveal that extraction efficiencies of TMPD and ALiCy systems were 93.8% and 72.3%, respectively. Moreover, different agents can be evaluated to strip boron from TMPD and ALiCy. The boron product and the extractants could then be generated and reused. Briefly, the environmental hazards caused by the desalination brine and boron resources can be reduced and circulated through this research with two different extraction systems.

Keywords: Boron, Desalination Brine, Solvent Extraction, Ionic Liquid Extraction, Resource Circulation

INTRODUCTION

Population increase has enhanced water demand in drinking, agriculture, and industry. Climate change also brings about a decrease in rainfall. Because of this growing water demand and declining rainfall, it has been reported that about 30% of people in the world will survive in areas with scarce water resources by 2025 [1]. To tackle this issue, alternative water supply methods, such as desalination, have been developed since the 1970s [2,3]. Desalination plants were initially constructed in Middle Eastern countries, Africa, and some Pacific Islands to generate freshwater. However, more and more countries now build desalination plants to save rainfall and groundwater. Although desalination technology is common now, the by-product of the desalination process, brine, has been known as a critical environmental contaminant due to its high salinity and high concentration of elements [4,5]. Brine deposal will increase the salinity of the coastal area, decrease the dissolved oxygen in the sea and affect the organism's habitat [6-8]. Furthermore, producing 1 liter of freshwater would generate 1 to 1.5 liter of brine through the distillation method and membrane process, demonstrating that the amount of brine from desalination plants is equal to or more than freshwater.

There are about 128 million m^3 of brine produced per day worldwide, and its treatment is a tricky problem [9]. Different strategies used to manage brine are direct disposal, minimization, and direct reuse [10-13]. To solve the disposal of desalination brine and reach the goal of resources circulation, the potential of brine utilization is explored to enhance the brine's value. One possible route is carbon capture [14-18]. Desalination brine consists of many elements which can be used for carbon capture, such as Na, Mg, and Ca. Their high concentrations make brine a significant resource for CO_2 mineralization. They can react with CO_2 and turn into sodium bicarbonate ($NaHCO_3$), magnesium carbonate ($MgCO_3$), and calcium carbonate ($CaCO_3$), which have applied value in many industries. The other possible route for brine treatment is resources circulation. Since there are many valuable elements such as lithium, rubidium, cesium, boron, uranium, and so on in the brine, some studies have tried different methods to recover them [19-27]. The recycling techniques are included in electrodialysis [19], ion-exchange [20,24,26,27], sorption [21], solvent extraction [22], ionic liquid extraction [23], chemical precipitation, and coagulation methodologies (The targeted elements and techniques are shown in Table 1). In this research, boron was selected to recover from brine to enhance the brine's value (The reason why we chose boron was that there are strict restrictions on the concentration of boron in fresh water. Therefore, boron would be enriched in desalination brine).

The average boron abundance now is below 0.005% in the earth, and the concentration in the ocean is less than 10 ppm. According to the U.S. Geological Survey (USGS), natural forms of boron ores are boric oxide (B_2O_3), ulexite ($NaCaB_5O_6(OH)_6{\cdot}5H_2O$), and dato-

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Table 1. Different techniques of recovering resources from brine [19-27]

Targeted element	Technique	References
Li	1. Electrodialysis through monovalent selective ion exchange membranes 2. Ion exchange through K2629, TP207 and TP208 resins	Guo et al. [19] Arroyo et al. [20]
Rb	1. Extraction by an integrated membrane distillation-selective sorption system 2. Solvent extraction through t-BAMBP	Naidu et al. [21] Chen et al. [22]
Cs	1. Ionic liquid extraction through t-BAMBP/C2mimNTf$_2$ 2. Ion exchange through Dowex 26 resin	Lee et al. [23] Lee et al. [24]
U	1. Adsorption through amidoxime adsorbents	Wiechert et al. [25]
B	1. Ion exchange through Amberlite IRA 743 resin 2. Ion exchange through Purolite S108, DIAION CRB03 and CRB05 resins	Lee et al. [26] Figueira et al. [27]

Table 2. Major boron reservoirs and their boron reserves [28]

Country	Reserve (t)
China	24,000
Chile	35,000
United States	40,000
Russia	40,000
Turkey	1,200,000

lite ($CaBSiO_4(OH)$) [28]. Boron has been employed in many industries from ancient times to the present. For instance, boron nitride (BN) has two polymorphs that can be utilized in many industries [29-31]. Hexagonal BN (α-BN) is a practical lubricant for transportation. The structure of cubic BN (β-BN) is like diamond, but the temperature resistance is higher than that of diamond. Boric acid (H_3BO_3), borax ($Na_2B_4O_7\cdot 10H_2O$), and boric oxide are commonly used in abrasives, pesticides, and antibiotics [32,33]. Because of the various applications of boron and its compounds, boron extraction is vital in many places.

Boron is mainly extracted from borate ores, currently. Nevertheless, borate ores are only located in some specific countries (Table 2), so it is difficult to acquire boron resources efficiently [28]. To address the lack of boron resources and environmental impacts in exploiting the process, boron was circulated from desalination brine through solvent extraction and ionic liquid extraction methods in this study. Solvent extraction is the process in which a specific element or compound is transferred from one solvent to another due to the difference in solubility or distribution coefficient between these two immiscible organic solvents [34,35]. Compared with other separation methods, it has a better separation effect, a higher degree of selectivity, and faster mass transfer. Moreover, solvent extraction has merits such as high throughput, easy continuous operation, and ease of automation. However, the common organic solvents in the solvent extraction system are high volatility, low thermal stability, and difficulty in recycling. To overcome these disadvantages, ionic liquids (ILs) are gradually applied in extraction techniques. ILs are usually made up of organic cations and inorganic or organic anions, and their melting points are generally below 100 °C [36,37]. Ionic-liquid extraction is a novel separation method which applies ILs as diluents and/or extractants for solvent extraction. Due to their low vapor pressure, high thermal stability, low flammability, and tunable characteristics, ILs, as a designer solvent, are replacements for volatile organic compounds in solvent extraction [38-40]. Nowadays, ILs are commonly applied to extract elements. For example, imidazolium-based ILs can extract Rb as extractants and diluents, and phosphonium-based ILs can extract Cd, Nd, and Ga under different conditions [41-44].

In this research, TMPD and ALiCy were chosen as the organic extractant and ionic liquid to recover boron from desalination brine. These two chemicals were applied in this study because of the merits of high selectivity, easy operation, and low cost. The parameters such as the initial pH value of the aqueous medium, the concentrations of TMPD and ALiCy, organic phase or ionic liquid phase/aqueous phase ratio (O/A or I/A ratio), contacting time, and reaction temperature were all explored. After extraction, the boron would be stripped back to the liquid phase through a suitable stripping agent, and the boron resources could then be reused. This study would demonstrate optimal conditions to recover boron from the desalination brine of each system. Through this research, it is expected to achieve the goal of circulating critical elements and protecting the environment (also conform to the goals of SDGs 17 such as "Clean water and sanitation (SDG 6)", "Responsible consumption and production (SDG 12)", and "Life below water (SDG 14)).

EXPERIMENTAL SECTION

1. Reagents and Chemicals

The brine used in this study was from the desalination plant based in Taiwan, and the concentrations of major elements after pretreatment are shown in Table 3. To extract boron from brine, TMPD and ALiCy were employed. TMPD (2,2,4-trimethyl-1,3-pentanediol, $C_8H_{18}O_2$, 97%) as an extractant was obtained from Sigma-Aldrich (St. Louis, MO, USA). Because TMPD is difficult to dissolve in kerosene directly, it was first dissolved in 2-ethylhexanol ($C_8H_{18}O$). The merit of 2-ethylhexanol is lower solvent loss than other common solvents. After being dissolved in 2-ethylhexanol, TMPD/2-ethylhexanol was then added into kerosene, and the ratio of 2-ethylhexanol and kerosene in this research was 30 : 70. 2-Ethylhexanol and kerosene were acquired from Alfa Aesar (Haverhill, MA, USA) and CPC Corporation (Kaohsiung, Taiwan), respectively. On the other hand, ALiCy as an ionic liquid was prepared by Aliquat

Table 3. The main elements in the brine and their concentrations

Elements	Na	Mg	Ca	K	B	Cs	Rb	Li
Concentration (mg/L)	21,216	2,247	916.5	792.6	43.1	40.2	35.4	14.3

336 (methyltrioctylammonium chloride, $C_{25}H_{54}ClN$, ≥97.0%) and Cyanex 272 (trihexyltetradecylphosphonium, $C_{48}H_{102}O_2P_2$, 90%) [45]. They were mixed with 1 M sodium bicarbonate ($NaHCO_3$, 99.9%) solution in a separatory funnel and shaken to produce ALiCy. In the process, Cl^- in Aliquat 336 and H^+ in Cyanex 272 was replaced by $NaHCO_3$. The whole reactions are shown in Eq. (1) [45]. Aliquat 336 and $NaHCO_3$ were from Alfa Aesar (Haverhill, MA, USA), and Cyanex 272 was from Sigma-Aldrich (St. Louis, MO, USA).

$$R_4NCl+HCy+NaHCO_3 \rightarrow R_4NCy+CO_2+NaCl+H_2O \tag{1}$$

Sodium hydroxide (NaOH, ≥98%) and sulfuric acid (H_2SO_4, 95-98%) were purchased from Honeywell (Charlotte, North Carolina, USA) to alter the pH value of brine. Moreover, sulfuric acid, nitric acid (HNO_3, 50-70%), hydrochloric acid (HCl, ≥36.5%), sodium hydroxide solution (NaOH, ≥98%), ammonia (NH_4OH, 30-33%), and deionized water (H_2O, resistivity 18.0 MΩ·cm) were from Honeywell (Charlotte, North Carolina, USA) for stripping procedure. In the analysis part, ICP multi-element standard solution was purchased from High-Purity Standards, Inc. (North Charleston, SC, USA) to investigate the boron concentration.

2. Apparatus

445 mm×730 mm×505 mm of funnel shaker (FS-12, Shin Kwang Precision Industry Ltd., New Taipei City, Taiwan) was used in this study to shake 250 mL of separating funnels at 600 rpm in the extraction process. The concentration of boron ion was analyzed by inductively coupled plasma optical emission spectrometry (ICP-OES, Avio 220 Max ICP-OES, PerkinElmer, Waltham, MA, America). The pH value was measured by pH meter (SP-2300, SUNTEX, New Taipei City, Taiwan). Both were calibrated initially to ensure the accuracy of values, and the relative standard deviation (RSD) of the ICP-OES and pH meter was below 2% and 1%, separately. The thermostatic bath (XMtd-204, BaltaLab, Vidzemes priekšpilsēta, Rīga, Latvia) was used to maintain the temperature during the whole separation process.

3. Extraction Process

TMPD was diluted into 2-ethylhexanol with kerosene, and ALiCy was diluted into kerosene to separate boron from desalination brine. The parameters included the initial pH value of the aqueous medium, the concentrations of TMPD and ALiCy, O/A and I/A ratios, contacting time, and reaction temperature were all investigated.

To calculate the efficiency of extraction, the distribution ratio and extraction percentage were used in this process. The distribution ratio, D, was the concentration ratio of the element in the organic phase to the element in the aqueous phase at equilibrium. The distribution ratio can be written as Eq. (2).

$$D=\frac{[M]_{org}}{[M]_{aq}}=\frac{C_i-C_f}{C_f}\times\frac{V_{aq}}{V_{org}} \tag{2}$$

C_i is the initial concentration of ions in the aqueous phase, and C_f is the equilibrium concentration of ions in the aqueous phase. V_{aq} and V_{org} are the volumes of the aqueous and organic phases.

Based on the distribution ratio, the extraction efficiency can be written as Eq. (3).

$$E_{ex}\,(\%)=\frac{D}{D+V_{aq}/V_{org}}\times 100 \tag{3}$$

D is the distribution ratio. V_{aq} and V_{org} are the volumes of aqueous and organic phases, separately.

4. Stripping Process

H_2SO_4, HNO_3, HCl, NaOH, NH_4OH, and H_2O were chosen as the stripping agents to strip boron from TMPD and ALiCy to the aqueous phase. The most suitable stripping agent was selected, and the parameters included concentration of stripping agent, O/A and I/A ratios, and contacting time was subsequently surveyed. The stripping efficiency is written as Eq. (4).

$$E_{st}\,(\%)=\frac{\Sigma M_{aq}}{\Sigma M_{org}}\times 100 \tag{4}$$

ΣM_{aq} is the concentration of ions in the aqueous phase after stripping, and ΣM_{org} is the ion concentration in the organic phase before stripping.

RESULTS AND DISCUSSION

1. Extraction Process-pH Value of the Aqueous Phase

The original pH value of brine was 8.3, so the initial values were set up from pH 8 to pH 14 in this study. Fixed parameters were 0.5 M TMPD and ALiCy, O/A and I/A ratios 1, contacting time for 15 mins, and reaction temperature at 298 K. Fig. 1 demonstrates that the suitable pH values for the two systems were different. In the TMPD system, the extraction efficiencies at pH 8 and 9 were above 90% but only 19.5% at pH 11. However, the extraction efficiency increased when the pH value was increasing in the ALiCy

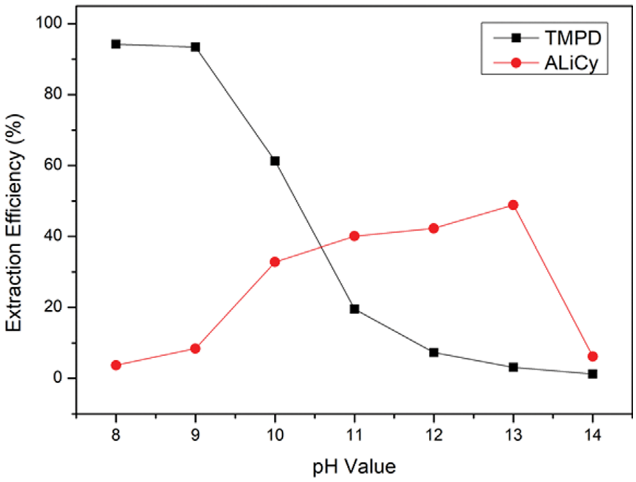

Fig. 1. Extraction efficiency of boron through two systems under different pH values.

system (Low extraction efficiency occurred at pH 14 because emulsification happened under strong basic conditions).

There are two reasons for the divergent phenomenon. To begin with, the extraction mechanisms of boron through TMPD and ALiCy are distinct. TMPD extracts H_3BO_3 [46], whereas ALiCy extracts $B(OH)_4^-$ under normal conditions [45] (Eqs. (5) and (6)). For this reason, the appropriate pH value would be different. Secondly, H_3BO_3 is a weak Lewis acid after hydrolysis when the pH value is above 9.23 (Eq. (7)) [45]. It means H_3BO_3 majorly exists at a pH value lower than 9.23, and $B(OH)_4^-$ is dominant at a higher pH value. This circumstance brings about TMPD efficiently extracting H_3BO_3 under pH value 9.23, and ALiCy efficiently extracting $B(OH)_4^-$ when the pH value is above 9.23. According to the above narrative, pH 8 and 11 were separately optimal in the TMPD and ALiCy systems because of high extraction efficiency and lower chemical usage, and the extraction efficiencies were 94.2% and 40.1%.

$$H_3BO_{3(aq)}+nTMPD_{(org)}\rightleftharpoons H_3BO_3\cdot nTMPD_{(org)}+aH_2O_{(aq)}+bH^+_{(aq)} \tag{5}$$

$$ALiCy_{(IL)}+H^+_{(aq)}+B(OH)^-_{4\,(aq)}\rightarrow ALiB(OH)_4\cdot HCy_{(IL)} \tag{6}$$

$$H_3BO_3+H_2O\rightleftharpoons B(OH_4)^-+H^+ \quad pKa=9.23 \tag{7}$$

2. Extraction Process-concentrations of TMPD and ALiCy

Once obtaining the optimal pH values, concentrations of TMPD and ALiCy were set from 0.1 M to 2 M. In the TMPD system, other fixed parameters were pH 8, O/A ratio 1, contacting time for 15 mins, and reaction temperature at 298 K. It can be found in Fig. 2 that above 90% of boron could be extracted by TMPD when its concentration was above 0.5 M, and the extraction efficiency reached equilibrium. Although extraction efficiency was a bit higher along with the rise in concentration, 0.5 M with 94.4% of extraction efficiency was chosen in this part due to less TMPD usage.

In the ALiCy system, fixed parameters were pH 11, I/A ratio 1, contacting time for 15 mins, and reaction temperature at 298 K. It can be noticed that ALiCy could not extract boron efficiently when the concentration of ALiCy was from 0.1 M to 0.5 M. Nevertheless, above 68% of boron could be extracted through 1 M, 1.5 M, and 2 M of ALiCy, and the reaction became equilibrated since the concentration was 1 M. To reduce the cost and usage amount of ALiCy, 1 M of ALiCy with 68.1% extraction efficiency was decided. Through comparison, it can be realized that the TMPD system has a higher extraction efficiency of boron than the ALiCy system under every concentration. Furthermore, the required concentration for equilibrium was lower than the ALiCy system, representing that the TMPD system can be applied for boron circulation from desalination brine with less chemical utilization.

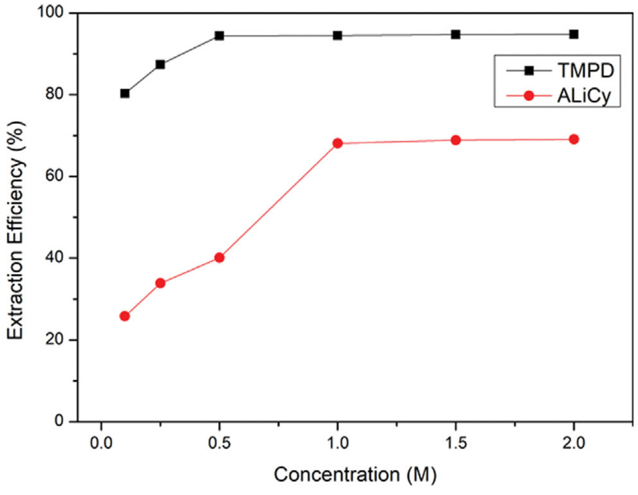

Fig. 2. Extraction efficiency of boron under different concentrations of TMPD and ALiCy.

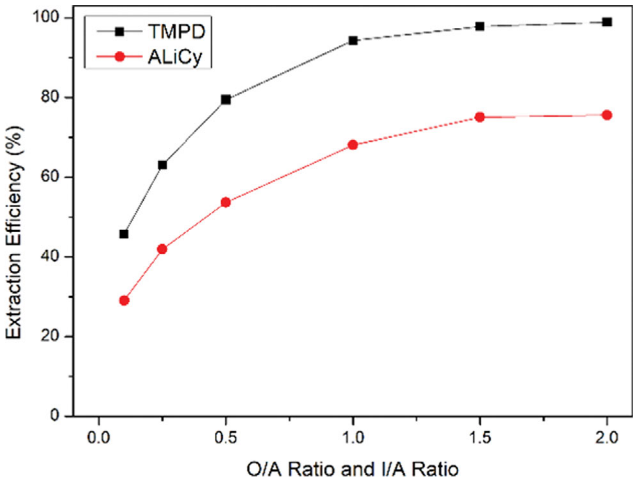

Fig. 3. Extraction efficiency of boron under different O/A and I/A ratios.

3. Extraction Process-O/A and I/A Ratios of TMPD and ALiCy

O/A and I/A ratios were adjusted from 0.1 to 2 in this part. The fixed parameters of the TMPD system were pH 8, 0.5 M of TMPD, contacting time for 15 mins, and reaction temperature at 298 K. The fixed parameters of the ALiCy system were pH 11, 1 M of ALiCy, contacting time for 15 mins, and reaction temperature at 298 K. In Fig. 3, it can be discovered that the extraction efficiency of boron in the TMPD system was above 90% when the O/A ratio was above 1. On the other hand, the extraction efficiency could reach above 68% when the I/A ratio was above 1. The results indicate that the insufficient organic extractant or ionic liquid cannot extract boron efficiently. Although higher O/A and I/A ratios could obtain more boron resources from brine, the boron concentration would reduce on account of more volume of TMPD and ALiCy. To lessen the extraction times, acquire more boron, and reduce the chemical usage, both O/A and I/A ratios 1 were selected. Under these conditions, the extraction efficiencies were 94.3 and 68.1%.

4. Extraction Process-contacting Time

Contacting time was regulated from 1 min to 60 mins in this research. The fixed parameters of the TMPD system were pH 8, 0.5 M of TMPD, O/A ratio 1, and reaction temperature at 298 K. The fixed parameters of the ALiCy system were pH 11, 1 M of ALiCy, I/A ratio 1, and reaction temperature at 298 K. As seen in in Fig. 4, boron extraction through the TMPD/kerosene system was rapid. 86.7% of boron could be extracted at 3 mins, and above 94% could be in the organic phase after reacting for 5 mins. The optimal contacting time of the TMPD/kerosene system was then opted for 5 mins to extract more boron (94.1%) and save time.

In the ALiCy system, the situation was different from the TMPD

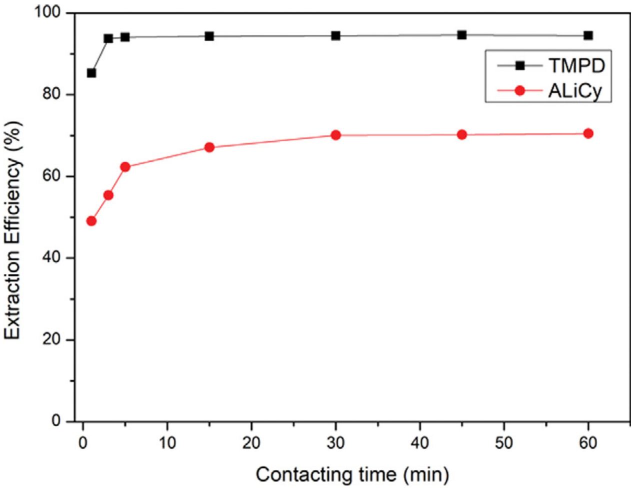

Fig. 4. Extraction efficiency of boron through two systems under different contacting time.

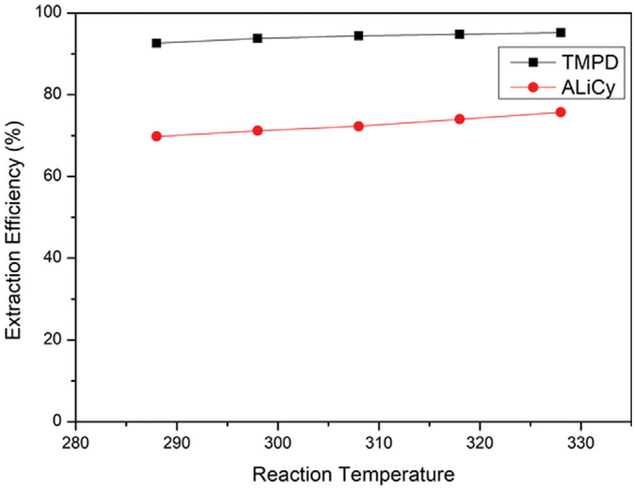

Fig. 5. Extraction efficiency of boron through two systems under different reaction temperatures.

system. The extraction efficiency was below 70% when the reaction time was 3 mins, 5 mins, and 15 mins, whereas 71.1%, 72.2%, and 73.1% at 30 mins, 45 mins, and 60 mins, respectively The surmised reason for this situation was that the viscosity of ALiCy was higher than most common ionic liquids and extractants, so it was challenging to mix with desalination brine thoroughly in the shaking funnel in a short period (Dynamic viscosities of ALiCy, common ionic liquids, and extractant are revealed in Table 4 [47-51]). Under this circumstance, 30 mins was chosen as the optimal contacting time in the ALiCy/kerosene system, and the extraction efficiency of boron was 71.1%.

5. Extraction Process-reaction Temperature

After the above data were acquired, reaction temperatures from 288 K to 328 K were investigated. The fixed parameters of the TMPD system were pH 8, 0.5 M of TMPD, O/A ratio 1, and contacting time for 5 mins. Fig. 5 demonstrates that the extraction efficiency of boron rose when the temperature increased (from 92.6% to 95.2% when the temperature went up from 288 K to 328 K). This result demonstrates that the boron extraction through TMPD is accessible at a higher temperature. Although a higher temperature could enhance the extraction ability of TMPD, 298 K with 93.8% of extraction efficiency was considered the suitable operating temperature in this system due to the lower energy consumption.

In the ALiCy system, the fixed parameters were pH 11, 1 M of ALiCy, I/A ratio 1, and contacting time for 30 mins. Fig. 5 displays that the boron extraction through ALiCy was advantageous at a higher temperature as well. The extraction efficiency increased when the temperature was from 288 K to 328 K (69.8% to 75.7%). Although the extraction efficiency was highest at 328 K in this study, 308 K was chosen as the optimal reaction temperature with 72.3% of extraction efficiency because of the energy saving.

To get more thermodynamics information, Fig. 6 reveals the linear relationship of log D with 1/T. On the basis of the slopes of the straight lines, the enthalpy change (ΔH) of the boron extraction through TMPD and ALiCy could be calculated using the van't Hoff equation (Equation 8). R in the equation is the ideal gas constant (8.314 J/mol*K), and ΔH were 8.7 kJ/mol and 6.3 kJ/mol, re- spectively. Positive ΔH means that the extraction reaction was endothermic, and a limited increase in the temperature was favorable for the reaction. Moreover, the Gibbs free energy (ΔG) could be obtained through Eq. (9). Since log D in Fig. 6 was all positive, ΔG was negative under every condition, representing that boron extraction through the TMPD and ALiCy systems was spontaneous from 288 K to 328 K.

In sum, the optimal extraction parameters of the TMPD/2-ethylhexanol+kerosene system were pH 8, 0.5 M of TMPD, O/A ratio 1, contacting time for 5 mins, and reaction temperature at 298K. The extraction efficiency was 93.8%, and it could reach 99% through two-stage extraction (Calculated through Eq. (10)). Besides, the optimal extraction parameters of the ALiCy/kerosene system

Table 4. Dynamic viscosity of ALiCy, common ionic liquids, and extractants [47-51]

Ionic liquid	ALiCy	$C_2mimNTf_2$	$C_4mimNTf_2$	Cyphos IL 101
Viscosity (mPa·S)	700-850	32.5	60.3	1,824
Extractant (Neutral)	TBP		Cyanex 923	
Viscosity (mPa·S)	3.41		40	
Extractant (Acidic)	PC88A	D2EHPA	Cyanex 272	Cyanex 301
Viscosity (mPa·S)	2.65	35.10	141	78
Extractant (Basic)	Alamine 336			
Viscosity (mPa·S)	78.6			

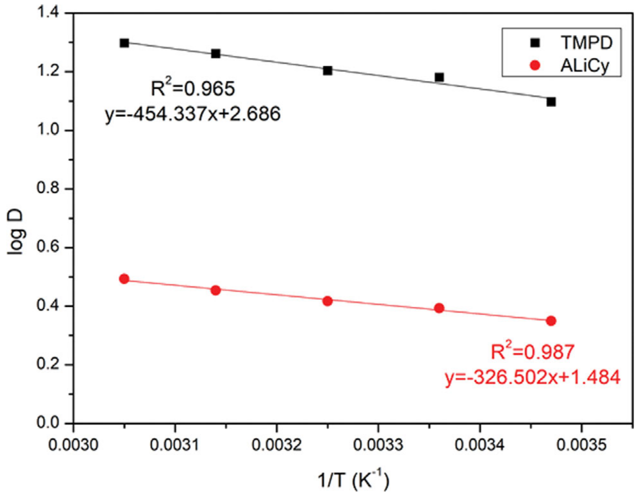

Fig. 6. The relationship of log D with 1/T.

were pH 11, 1 M of ALiCy, I/A ratio 1, contacting time for 30 mins, and reaction temperature at 308 K. The extraction efficiency was 72.3%, and it could reach 99% through four-stage extraction. The speculation the ALiCy system had lower extraction efficiency overall may be the difference in extraction mechanism or the synthesis of ALiCy was not completed. Therefore, the impurities in ALiCy disrupt the extraction reaction. In further work, if the characteristics of ALiCy can be analyzed comprehensively, the extraction efficiency may be enhanced.

$$\log D = -\frac{\Delta H}{2.303RT} + C \tag{8}$$

$$\Delta G = -2.303RT\log D \tag{9}$$

$$n = \frac{\log(100-E_{99})-2}{\log(100-E_x)-2} \tag{10}$$

6. Stripping Process-selection of Stripping Agent

After the extraction process, 40.4 mg/L and 31.2 mg/L of boron were separately in the TMPD and ALiCy phases. To make the boron resources be in the aqueous phase, different stripping agents were surveyed. The stripping agents selected in this research were H_2SO_4, HNO_3, HCl, NaOH, NH_4OH, and H_2O. The fixed parameters were concentrations of 1 M, O/A and I/A ratios 1, and stripping time for 15 mins. It can be found in Fig. 7 that the stripping efficiency of boron through NaOH and NH_4OH was higher than through acids and water in the TMPD system. The conjectured reason was that alkaline solutions could make H_3BO_3 turn into $B(OH)_4^-$, so TMPD could not efficiently extract H_3BO_3 in the organic phase (Eq. (5)).

On the other hand, both acids and alkaline solutions were effective for the stripping process in the ALiCy system. The presumed reason was that acids would reduce the pH value of the system, causing $B(OH)_4^-$ and H^+ to become H_3BO_3. ALiCy could then not extract $B(OH)_4^-$ in the ionic liquid phase. Nonetheless, OH^- from NaOH and NH_4OH would exchange $B(OH)_4^-$ which was in $ALiB(OH)_4 \cdot HCy$, and form H_2O with H^+ from HCy. These consequences demonstrate that the stripping behavior in the ALiCy system was different through acids and alkaline solutions.

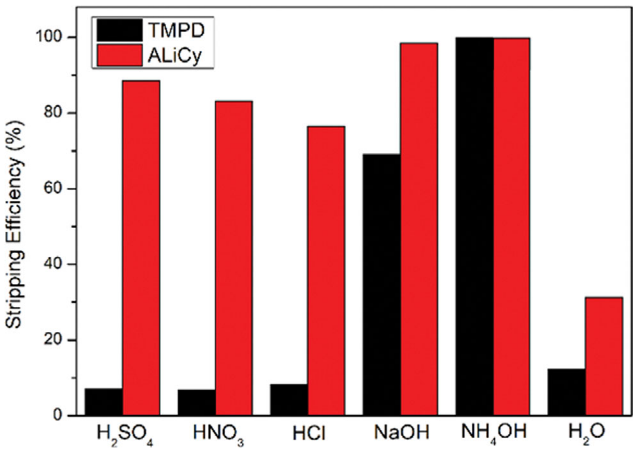

Fig. 7. Stripping efficiency of boron through different stripping agents.

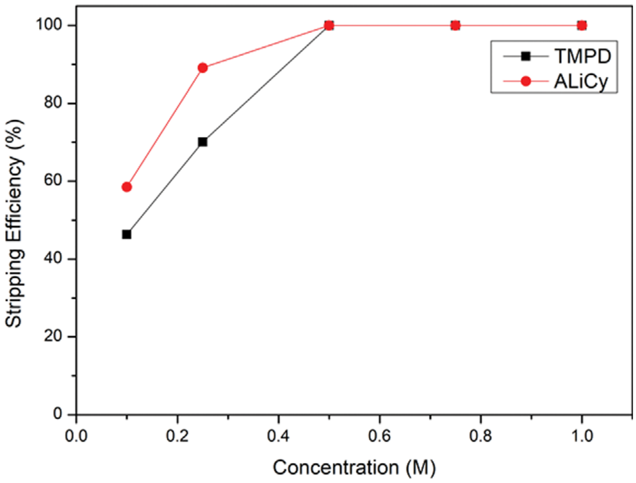

Fig. 8. Stripping efficiency of boron under different concentrations of NH_4OH.

In accordance with the above results, NH_4OH was chosen as the suitable agent in both systems due to low cost and high stripping efficiency (also easy to compare). The concentrations of NH_4OH, stripping O/A and I/A ratios, and stripping time will be explored in follow-up procedures.

7. Stripping Process-concentration of NH_4OH

Upon confirming the suitable stripping agent, its concentration (0.1 M to 1 M) was then surveyed. The fixed parameters were O/A and I/A ratios 1 and stripping time for 15 mins. Fig. 8 displays that the trends of stripping efficiency in the two systems was similar. 0.1 M and 0.25 M of NH_4OH could not efficiently strip boron resources back to the aqueous phase (below 90%), whereas 0.5 M to 1 M of NH_4OH could completely strip boron. It indicated that sufficient NH_4OH was needed in the stripping process. 0.5 M of NH_4OH was selected in both systems to save chemical usage and cost.

8. Stripping Process-stripping O/A and I/A Ratios

O/A and I/A ratios were set up as 0.5, 2/3, 1, 2, 4, and 10 (reciprocal of ratio in the extraction process). Fixed parameters were

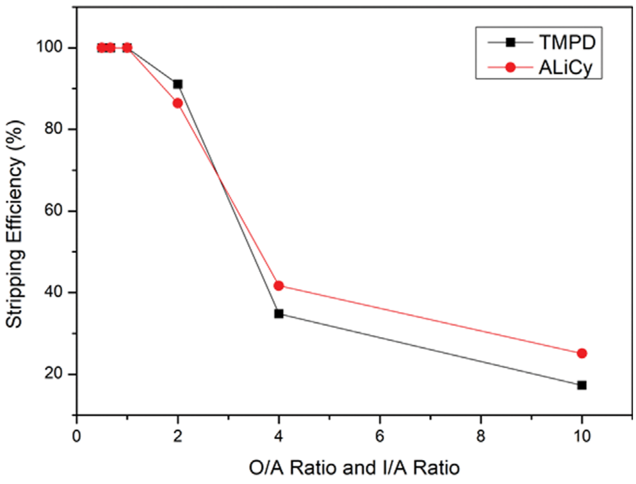

Fig. 9. Stripping efficiency of boron under different O/A and I/A ratios.

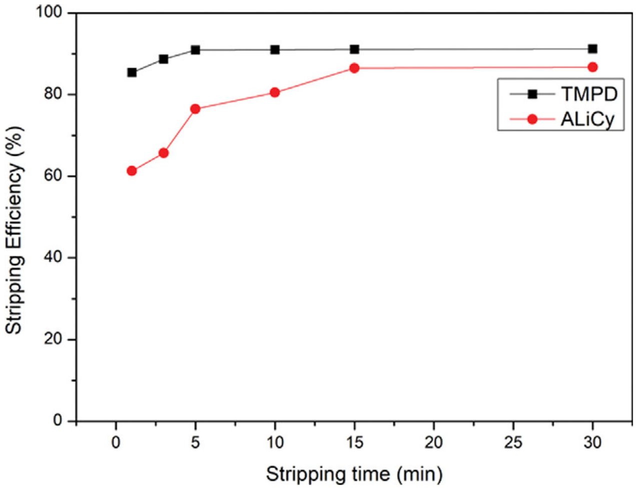

Fig. 10. Stripping efficiency of boron under different stripping time.

0.5 M of NH_4OH and stripping time for 15 mins. Fig. 9 shows that the stripping efficiency of the TMPD system was 100% when the O/A ratios were 0.5, 2/3, and 1, whereas the efficiency decreased when the ratios were from 2 to 10, indicating that enough NH_4OH was beneficial to the stripping process. Although the stripping process was only 91.1% when the O/A ratio was 2, the boron concentration could be enriched twice due to the half volume of NH_4OH. Hence, O/A ratio 2 was known as the optimal parameter in the TMPD system.

In the ALiCy system, the condition was similar. The stripping efficiency was 100% when the ratios were 0.5, 2/3, and 1, whereas 86.4%, 41.7%, and 25.1% when the ratios were from 2 to 4. The chosen I/A ratio was 2 as well to reduce the consumption of NH_4OH, and a small amount of NH_4OH can be added to improve stripping efficiency if needed. Although lower ratios in the two systems could enrich more boron resources, it needed multi-stage stripping or additional NH_4OH to enhance stripping efficiencies and avoid boron loss. However, multi-stage extraction or adding NH_4OH would increase the usage of NH_4OH. On second thought, ratio 2 was more suitable.

9. Stripping Process-stripping Time

1 min to 30 mins of stripping time was investigated, and other fixed parameters were 0.5 M of NH_4OH and ratios 2. Fig. 10 denotes that the stripping behavior through NH_4OH in the TMPD system was very rapid. It could strip 85.4% of boron for 1 min and get equilibrium for 5 mins. However, the reaction in the ALiCy system was slower. It needed 15 mins to reach equilibrium, and the primary reason was the same as in the extraction part: the viscosity of ALiCy was high, so it needed more time to agitate with NH_4OH thoroughly.

To summarize, the optimal stripping parameters of the TMPD/2-ethylhexanol+kerosene system were 0.5 M of NH_4OH, O/A ratio 2, and contacting time for 5 mins. Furthermore, the optimal stripping parameters of the ALiCy/kerosene system were 0.5 M of NH_4OH,

Table 5. Comparison of this study with the previous research [45,46,52,53]

Author & Year	Main point
This article	Employing TMPD and ALiCy to circulate boron from desalination brine. Under the optimal parameters, the extraction efficiencies were 93.8% and 72.3%, and the stripping efficiencies were 90.9% and 86.5%.
Guo et al. [52]	0.68 M of TMPD, 30% (v/v) 2-ethylhexanol, pH 1.55, reaction temperature at 298.15 K, and O/A ratio 1 were the optimal extraction parameters from lithium-rich brine. 0.2 M of NaOH with O/A ratio 0.5 were conducted in the stripping process. The overall extraction and stripping efficiency by two-stage operation could reach 99.95% and 99.99%
Peng et al. [46]	pH<7, O/A=1, and TMPD/H_3BO_3 molar ratio of 2 : 1 was ideal for boron recovery from unacidified salt lake brine. Under these conditions, the extraction efficiency of boron was >85%. In the stripping process, NaOH was selected, and the stripping efficiency of H_3BO_3 increased with the mounting of NaOH concentration.
Fortuny et al. [45]	Boron was extracted from chloride media. The optimal equilibrium pH value of the aqueous phase was pH 8-9, and the reaction was ideal when the contacting period was extended in the extraction part. Moreover, 0.2 M of NaOH with I/O ratio 1 could strip boron back to the aqueous phase.
Coll et al. [53]	About 60% of boron could be extracted from high chloride medium under a wide pH range through 0.54 M of the ALiCy in 10% decanol/kerosene.

Table 6. Purity analysis of $NH_4B_5O_8 \cdot 4H_2O$ in the TMPD system

Element	$NH_4B_5O_8 \cdot 4H_2O$	Na	K	Mg, Ca, Cs, Rb, Li, Cu
Purity (%)	99.88	0.07	0.05	Not detected

Table 7. Purity analysis of $NH_4B_5O_8 \cdot 4H_2O$ in the ALiCy system

Element	$NH_4B_5O_8 \cdot 4H_2O$	Na	K	Mg, Ca, Cs, Rb, Li, Cu
Purity (%)	99.6	0.23	0.17	Not detected

I/A ratio 2, and contacting time for 15 mins. Under these conditions, the stripping efficiency was 90.9% and 86.5%, respectively.

10. Comparison and Analyses

As soon as boron was circulated from desalination brine through the TMPD/2-ethylhexanol+kerosene and ALiCy/kerosene systems, the parameters and results were compared with the previous research (Table 5). It can be noticed that above 85% of H_3BO_3 could be extracted through a lower concentration of TMPD under pH<9.23, and NH_4OH and NaOH were the practical stripping agents. The efficiencies among the three researches were slightly different because the initial concentration of boron, original media, and some operational conditions were distinct.

On the other hand, it can be found that the initial pH>9.23 of the aqueous phase is the suitable condition for boron extraction through the ALiCy system (H_3BO_3 will turn into $B(OH)_4^-$), and the contacting time should be longer to ensure the reaction is completed. In the stripping process, NaOH was selected in other studies, and most boron could be stripped back to the aqueous phase (NH_4OH was chosen in this research due to its low cost).

Through the above comparison, it can be realized that the TMPD and ALiCy systems are steady and have high extraction ability for boron extraction. As long as the parameters are adjusted, they can still be applied in different situations.

After extracting and stripping boron through TMPD, ALiCy, and NH_4OH, ammonium pentaborate ($NH_4B_5O_8 \cdot 4H_2O$) would be acquired, and the purities through the two systems are shown in Tables 6 and 7. In addition to $NH_4B_5O_8 \cdot 4H_2O$, B_2O_3 could be generated by heating $NH_4B_5O_8 \cdot 4H_2O$, and H_3BO_3 could be formed through the reaction of B_2O_3 with water if people need extensive application.

In a nutshell, this research utilized two systems to recover boron resources from desalination brine. The two systems could not only reduce the environmental hazards caused by brine but also increase the value of brine and supply boron products. Through this experience, more resources may be efficiently circulated from brine in the future to reach the fulfillment of the 17 United Nations Sustainable Development Goals.

CONCLUSION

This research applied the TMPD and ALiCy systems to recover boron from desalination brine. The results reveal that the extraction parameters of the TMPD system were pH 8, 0.5 M of TMPD, O/A ratio 1, contacting time for 5 mins, and temperature at 298 K; the stripping parameters were 0.5 M of NH_4OH, O/A ratio 2, and reaction for 5 mins. Under these conditions, the extraction and stripping efficiencies were 93.8% and 90.9%. The extraction parameters of the ALiCy system were pH 11, 1 M of ALiCy, I/A ratio 1, contacting time for 30 mins, and temperature at 308 K; the stripping parameters were 0.5 M of NH_4OH, I/A ratio 2, and reaction for 15 mins. Under these circumstances, the extraction and stripping efficiencies were 72.3% and 86.5%. In conclusion, the boron extraction from desalination brine through TMPD and ALiCy systems are prospective methods to achieve the goal of the circular economy, resources circulation, and environmental protection. If more resources can be circulated from brine and the procedures can be improved, then from disposal to utilization will become the trend in the future.

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NOMENCLATURE

D : distribution ratio
$[M]_{org}$: the concentration of ions in the organic phase after extraction
$[M]_{aq}$: the concentration of ions in the aqueous phase after extraction
C_i : initial concentration of ions in the aqueous phase
C_f : equilibrium concentration of ions in the aqueous phase
V_{aq} : the volume of the aqueous
V_{org} : the volume of the organic phases
E_{ex} : extraction efficiency
E_{st} : stripping efficiency
ΣM_{aq} : the concentration of ions in the aqueous phase after stripping
ΣM_{org} : the ions concentration in the organic phase before stripping
ΔH : enthalpy change
R : ideal gas constant (8.314 J/mol*K)
T : temperature in Kelvin scale
ΔG : Gibbs free energy change

AUTHOR CONTRIBUTIONS

Conceptualization, C. H. Lee; methodology, C. H. Lee and W. S. Chen; validation, C. H. Lee and W. C. Chen; formal analysis, C. H. Lee; investigation, C. H. Lee; data curation, W. S. Chen; writing—original draft preparation, C.-H. Lee; writing—review and editing, C. H. Lee and W. C. Chen; visualization, C.-H. Lee; supervision, W. S. Chen. All authors have read and agreed to the published version of the manuscript.

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Data Availability Statement

Not applicable.

Conflicts of Interest

There are no conflicts to declare.

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