

Recovery of boron from desalination brine through Amberlite IRA 743 resin

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ABSTRACT

Boron has a high applied value from the past to now. It can be used in composite material, aerospace industry, semiconductor industry, and many other areas. Nonetheless, boron resources are only located in some countries, so it is strenuous to acquire. To obtain more boron and reach the goal of resources circulation, boron was recovered from the desalination brine through Amberlite IRA 743 resin in this study. Because extreme climate change makes people have insufficient fresh-water, desalination technology has matured since the 20th century. Although it can cope with fresh-water scarcity, the by-product, brine, is detrimental to the environment. The only merit of brine is that it is a concentrated solution, so the boron concentration in brine is higher than in some ores. This recovering system then uses the characteristics of brine to get boron. The research could be divided into three parts. First, the adsorption isotherm model was investigated, and the saturated adsorption capacity of boron through Amberlite IRA 743 resin was 74.34 mg/g and conformed to the Langmuir model. The second part surveyed the optimal parameters of boron adsorption through Amberlite IRA 743 resin. The results revealed that 18.9 mg/L of boron could be fully adsorbed from brine under pH 10, L/S ratio of 200, contacting period of 128 min, and temperature at 328 K. On the other hand, different agents would be tested to desorb the boron from the resin, and the boron product could be generated. In a nutshell, through this research, people can reduce the side effect of brine and circulate boron resources in an eco-friendly method.

Keywords: Boron; Ion exchange; Amberlite IRA 743; Desalination; Brine; Recovery; Resources circulation

1. Introduction

Boron, the first element in the boron family (group 13) of the periodic table, has an atomic number of 5, an atomic weight of 10.80, a melting point of 2,076°C, and a boiling point of 3,927°C. Boron was discovered by Humphry Davy and Joseph Louis Gay-Lussac from the borax ($\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$) and boric acid (H_3BO_3) [1,2]. They initially named it boracium in Aladdin because it was extracted from borax. The average abundance of boron is 0.001% in the Earth's crust, and its concentration in the ocean is 4–5 mg/L. Based on the report of the U.S. Geological Survey (USGS), elemental boron does not

occur in nature [3]. Boron combines with oxygen and other elements to form boric acid or borates. Natural forms of boron ores are ulexite ($\text{NaCaB}_5\text{O}_6(\text{OH})_6 \cdot 5\text{H}_2\text{O}$), boric oxide (B_2O_3), and datolite ($\text{CaBSiO}_4(\text{OH})$), and their significant reservoirs are shown in Table 1 [3].

Boron has high applied value in many industries from the past to now. Elemental boron can be turned into boron fiber and used in the composite material, the aerospace industry, golf clubs, and fishing rods [4,5]. It can also be a dopant in the semiconductor industry [6]. Besides, the boron compounds are also practical. For example, borane can be the rockets' high energy fuel (HEF), and magnesium diboride (MgB_2) is a superconductor at a low temperature

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[7–9]. Boron nitride (BN) has many polymorphs and can be used in many areas [10–14]. For example, hexagonal BN (α -BN) is a practical lubricant for motorcycles and cars. The structure of cubic BN (β -BN) is similar to diamond, but its temperature resistance is better than diamond. Boric acid (H_3BO_3) is commonly used in abrasives, cleaning products, pesticides, and antibiotics [15,16]. On the other hand, the dominant utilizers of boron resources are the glass and ceramics industries, which account for 80% of total borate consumption in the United States [3]. Due to the limitless application of boron and its compounds, boron extraction was crucial in many countries.

Currently, boron is mainly extracted from borate ores. However, borate ores are only located in some countries, so it is challenging to obtain boron resources efficiently. To figure out the problems of lack of boron resources and environmental hazards in the exploiting process, boron was recovered from waste desalination brine in this study. Because of the greenhouse effect and global warming, extreme climate change makes people have insufficient freshwater. Based on the investigation of the United Nations, above 1 billion people in the world will survive in areas with scarce water resources by 2025 [17]. In response to freshwater scarcity, seawater desalination technology has developed since the beginning of the 20th century [18]. Although freshwater can be acquired from desalination technology, the by-product, brine, will decrease the concentration of dissolved oxygen in seawater and affect the organism's habitat. Besides, the amount of brine from desalination plants is equal to the freshwater, demonstrating that the more freshwater is obtained, the more brine is dumped back into the sea. Nevertheless, there is also an advantage of brine. Because brine is a concentrated solution, the metal concentrations in brine are higher than in seawater and some ores. If brine could be appropriately applied, many metals could be recovered to reduce environmental damage and achieve a circular economy. Due to this reason, some methods have already been explored by our group to create the applied value of brine [19,20].

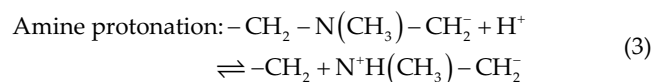
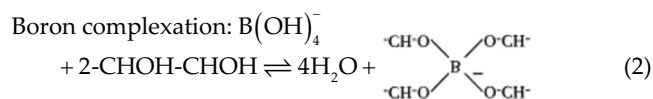
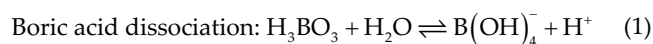
Ion exchange resins are widely used to recover or remove boron from wastes and drinking water. Among all the resins, the resins with N-methyl-d-glucamine (NMDG) functional groups (possesses polyols and tertiary amine ends) can provide more opportunities for complexation reaction with boron. The common resins include Diaion WA30, Diaion CRB 02, Purolite S108, Dowex 2X8, Dowex XUS 43594.00, Amberlite IRA 743, XSC-700 are all modified by NMDG functional group [21,22]. Amberlite IRA

743 resin, a boron-specific resin, has been researched to remove boron from wastewater and drinking water in numerous studies [23–34]. Due to its high affinity for boron, this research aims to utilize Amberlite IRA 743 resin in the batch system to recover boron from desalination brine. The study consists of three parts. To begin with, the adsorption isotherms, described by means of the Langmuir and Freundlich isotherms, were used to investigate the ion exchange behaviors of boron. Next, the optimal parameters of boron adsorption, such as pH value, liquid–solid ratio (L/S ratio), and contacting period, were surveyed. In addition, the thermodynamic parameters like enthalpy, entropy, and Gibbs free energy would also be explored throughout the boron adsorption to realize how the reaction was processed. Finally, conduct boron desorption batch tests in the aqueous phase by six different chemicals, namely, sulfuric acid (H_2SO_4), nitric acid (HNO_3), hydrochloric acid (HCl), sodium hydroxide solution (NaOH), ammonia (NH_4OH), and DI water (H_2O). Boron product could then be generated after the desorption process. In a nutshell, this study demonstrates the experimental parameters of boron adsorption through Amberlite IRA 743 resin and reveals that boron in waste brine could turn into resources with the goal of laboratory-safe, low-cost, and energy efficiency.

2. Materials and methods

2.1. Reagents and chemicals

Amberlite IRA 743 resin was purchased from Sigma-Aldrich (St. Louis, MO, USA) to adsorb boron from desalination brine in this study. Amberlite IRA 743 resin is a weakly basic anion exchange resin with macroporous polystyrene matrix on which N-methylglucamine (free base form) functional group is attached [24,27]. The appearance, chemical structure, and basic information of Amberlite IRA 743 resin are shown in Fig. 1a, b, and Table 2, respectively. It is realized that boron is retained based on Eqs. (1)–(3). The borate ion is complexed by two sorbitol groups, and a proton is retained by a tertiary amine through an anion exchange mechanism [23,25].



Boron oxide (B_2O_3 ; 99%) was acquired from Sigma-Aldrich (St. Louis, MO, USA) and dissolved in DI water (resistivity 18.0 M Ω .cm). The adsorption models were investigated with Amberlite IRA 743 resin and boron oxide solutions. Once the adsorption model was available, the resin was contacted with desalination brine to conduct

Table 1
Major reservoirs of boron [3]

Country	Reserve (t)
Peru	4,000
China	24,000
Chile	35,000
United States	40,000
Russia	40,000
Turkey	1,100,000

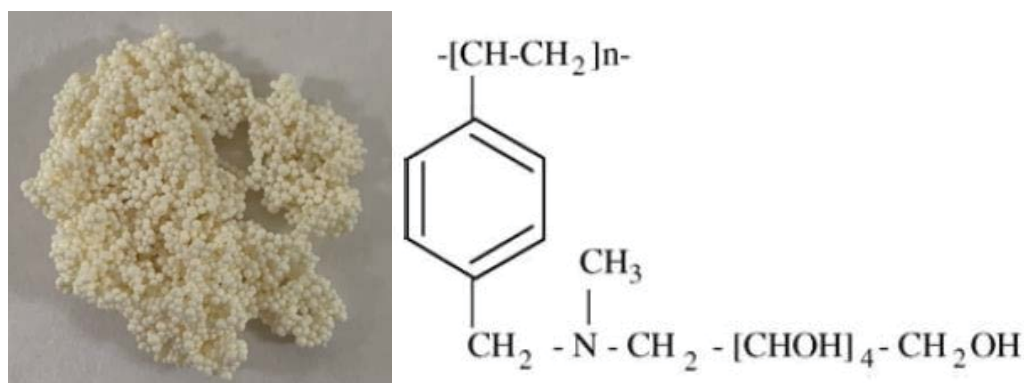


Fig. 1. (a) Appearance and (b) chemical structure of Amberlite IRA 743 resin.

Table 2
Basic information of Amberlite IRA 743 resin

Amberlite IRA 743 resin	Basic information
Physical form	Off-white, opaque, spherical beads
Description	Weakly basic anion exchange resin
Particle diameter	500–700 μm
Density (g/cm^3)	0.68 [23,24]
Moisture (%)	48–54
pH range	0–14 [23,24]
Matrix	Styrene-divinylbenzene (macroporous)
Matrix active group	N-methylglucamine (free base form) functional group
Type	Chelant
Total exchange capacity	≥ 0.6 eq/L

the experiment of the pH value, liquid-solid ratio (L/S ratio), contacting period, and thermodynamics. The brine was from the desalination plant based in Taiwan, and the concentration of key elements are shown in Table 3 [35]. Sodium hydroxide (NaOH ; $\geq 98\%$) and sulfuric acid (H_2SO_4 ; 95%–98%) were both obtained from Honeywell (Charlotte, North Carolina, USA) to alter the pH value for testing the optimal parameter. Moreover, sulfuric acid (H_2SO_4 ; 95%–98%), nitric acid (HNO_3 ; $\geq 65\%$), hydrochloric acid (HCl ; $\geq 36.5\%$), sodium hydroxide solution (NaOH ; $\geq 98\%$), ammonia (NH_4OH ; 30%–33%) were also bought from Honeywell (Charlotte, North Carolina, USA) for desorption procedure. In the analysis part, ICP multi-element standard solution were purchased from High-Purity Standards, Inc. (North Charleston, SC, USA). The nitric acid was diluted to 1% to be the background value and thinner for ICP analysis.

2.2. Apparatuses

In this experiment, the main apparatuses are inductively coupled plasma optical emission spectrometry (ICP-OES, Varian, Vista-MPX, PerkinElmer, Waltham, Massachusetts State, America), pH meter (SP-2300; SUNTEX; New Taipei City, Taiwan), and the thermostatic bath (XMtd-204; BaltaLab, Latvia). ICP-OES was used to determine the concentration of boron ion and other ions. The relative standard deviation (RSD) was below 2%. The pH meter in this

Table 3
Concentration of key elements in desalination brine in Taiwan [35]

Elements	Concentration (mg/L)
Na	17,420
Mg	2,112
K	782.6
Ca	722.2
Rb	36.4
Li	19.5
B	18.9

experiment was used to determine the pH value, and the RSD was below 1%. Both were calibrated before experiments to ensure the accuracy of values. On the other hand, the thermostatic bath was used to maintain the temperature during the whole process.

2.3. Ion exchange process

Amberlite IRA 743 resin was first contacted with boron oxide solutions to explore the adsorption isotherm model. To realize how Amberlite IRA 743 resin adsorbed boron, it was added into solutions of different initial boron

concentrations (10, 20, 50, 100, 250, 400, and 600 mg/L) for 1,024 min. The relationship between C_e (concentration of adsorbate in the liquid when adsorption is in equilibrium) and q_e (equilibrium adsorption capacity of the adsorbent) will be discussed in Section 3. In this study, two empirical isotherm models, Langmuir and Freundlich isotherms, which were widely used to describe the adsorption behavior, were also applied to fit with boron adsorption through Amberlite IRA 743 resin. Eqs. (4) and (5) are the Langmuir equation and Freundlich equation, respectively [36–38]. In the Langmuir equation, the maximum adsorption capacity q_m and adsorption equilibrium constant K_L could be obtained by the relationship between C_e and C_e/q_e . As for the Freundlich equation, empirical constant n , and the adsorption equilibrium constant K_F could be calculated from the relationship between $\ln C_e$ and $\ln q_e$.

$$\frac{C_e}{q_e} = \frac{C_e}{q_m} + \frac{1}{q_m K_L} \quad (4)$$

$$\ln q_e = \ln K_F + \frac{1}{n} \ln C_e \quad (5)$$

Once confirmed the isotherm model of boron adsorption through Amberlite IRA 743 resin was, the resin was reacted with desalination brine to recover boron resources. The parameters set up in the batch system included pH value (9–14), liquid–solid ratio (100–1,000), and contacting period (2–1,024 min). Besides, to perform a thermodynamic analysis, Amberlite IRA 743 resin was contacted with desalination brine under the conditions of 288 to 328 K. In compliance with the results, the slope and intercept of the figure could be achieved. Enthalpy, entropy, and Gibbs free energy could then be calculated by Eqs. (6)–(10). Among the equations below, R is the ideal gas constant, 8.314. K_d is the partition coefficient when the adsorption was equilibrated. C_i and C_f represent the concentration of boron in the solution before adsorption and after adsorption. V and M are the volume of solution and the molarity of resin, separately.

$$\Delta H = \text{Slope} \times R \quad (6)$$

$$\Delta S = \text{Intercept} \times R \quad (7)$$

$$\Delta G : -RT \ln K_d \quad (8)$$

$$K_d = \frac{C_i - C_f}{C_i} \times \frac{V}{M} \quad (9)$$

$$\ln K_d = \frac{\Delta S}{R} - \frac{\Delta H}{RT} \quad (10)$$

Sulfuric acid (H_2SO_4), nitric acid (HNO_3), hydrochloric acid (HCl), sodium hydroxide solution (NaOH), ammonia (NH_4OH), and DI water (H_2O) were tested in the desorption

process to determine the most suitable agent to desorb boron from the resin to the aqueous solutions. The boron product could be further produced after evaporating the solutions to reach the goal of resources circulation.

3. Results and discussion

3.1. Adsorption isotherm model of Amberlite IRA 743 resin

To get the isotherm model, Amberlite IRA 743 resin was added into different initial concentrations of boron oxide solutions (10, 20, 50, 100, 250, 400, 600 mg/L) under the conditions of L/S ratio of 1,000 for 1,024 min at 298 K. Fig. 2 illustrates the relationship between C_e (concentration of adsorbate in the liquid when adsorption is in equilibrium) and q_e (equilibrium adsorption capacity of the adsorbent). Based on the figure, the saturated adsorption capacity of boron through Amberlite IRA 743 resin was about 70 mg/g.

After obtaining the estimated value, Eqs. (4) and (5) were applied to generate the Langmuir model and Freundlich model, respectively. The q_m (saturated adsorption) and K_L (adsorption equilibrium constant) in the Langmuir equation could be calculated with slope and intercept from Fig. 3. n (empirical constant) and K_F (adsorption equilibrium constant) in the Freundlich equation could be acquired from Fig. 4 as well. All the calculated processes and values are demonstrated in Table 4. Moreover, Fig. 3 reveals that the R^2 was 0.99737 in the Langmuir model, and Fig. 4 illustrates that the R^2 was 0.83485 in the Freundlich model. A higher R^2 of the Langmuir model indicated a better fit for boron adsorption through Amberlite IRA 743 resin. It also denoted that the resin has a uniform adsorption position on the surface and the accurate saturated adsorption capacity was 74.34 mg/g. Besides, the comparison of Amberlite IRA 743 resin with other resins are shown in Table 5. It demonstrates that Amberlite IRA 743 resin could adsorb more boron than other resins. The reasons may be that the conditions of the adsorbing process, the surface area of resins, the particle size of adsorbents, pore size distribution, and molecular polarity were different.

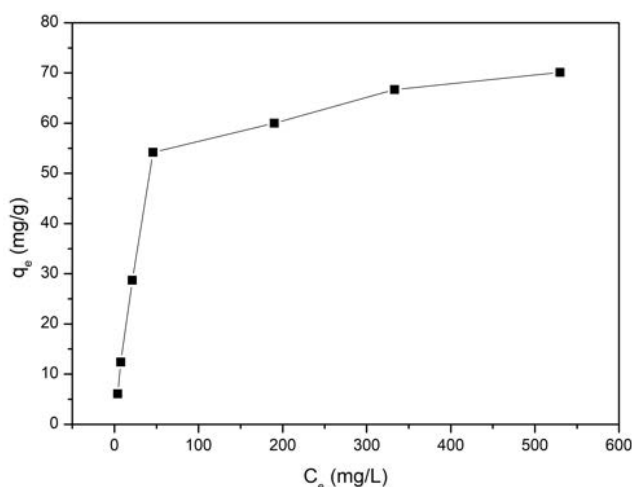


Fig. 2. Adsorption capacity of boron through Amberlite IRA 743 resin.

3.2. Adsorption of boron from desalination brine – effect of initial pH value

Although there were many metal ions in the brine, most of them would not affect the exchange process. The reason is that Amberlite IRA 743 resin is a weakly basic anion exchange resin, which cannot adsorb Na, Mg, K, Ca, Rb, and Li. (They are all cation in the brine.) Therefore, they were not detected after ion exchange in this research.

Because the pH value of brine was 8.14, the initial values were set up from pH 9 to pH 14. Other parameters were fixed as followings: the L/S ratio of 1000, contacting time of 1,024 min, and temperature at 298 K. Fig. 5 illustrates that the initial pH value played an essential role in boron adsorption, and there are two emphases in this part. First, the distributions of $B(OH)_3$ and $B(OH)_4^-$ are controlled by the pH value of the solution, which significantly affects the recovery of boron from aqueous solutions. According to the previous study, the tetrahedral ions ($B(OH)_4^-$) become dominant species with a pH within the range of 9 and 10 [45]. It means that $B(OH)_4^-$ could start to be adsorbed at pH

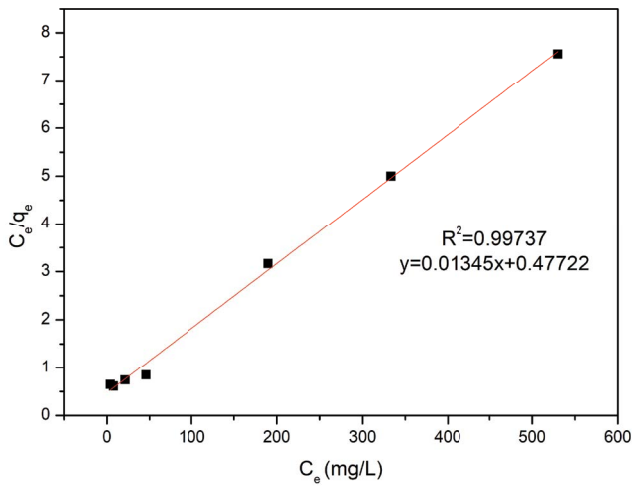


Fig. 3. Adsorption capacity of boron through Amberlite IRA 743 resin (Langmuir model).

between 9 and 10. Second, the adsorption capacities were lower when pH values increased from pH 10 to pH 14. The speculated reason is that a higher pH value inhibited Amberlite IRA 743 resin from releasing OH^- to exchange $B(OH)_4^-$, so the adsorption capacities decreased when pH increased. For the above reasons, the optimal pH value was 10, and the adsorption capacity was 9.39 mg/g in this study.

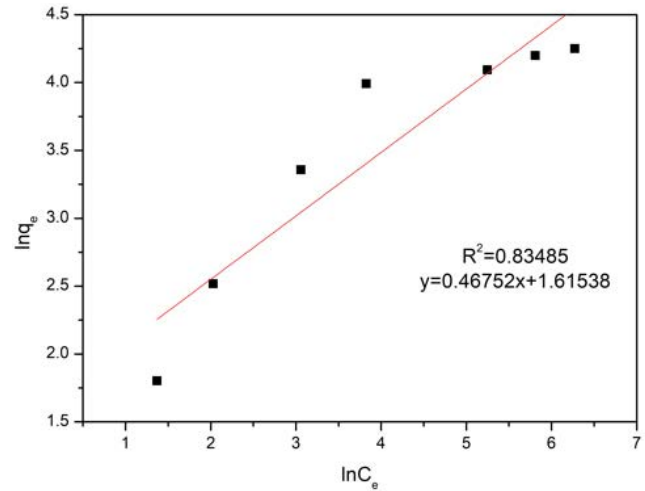


Fig. 4. Adsorption capacity of boron through Amberlite IRA 743 resin (Freundlich model).

Table 4
Details of Langmuir and Freundlich model

Langmuir model ($R^2 = 0.99737$)	Freundlich model ($R^2 = 0.83485$)
$q_m = 1/\text{slope}$	$n = 1/\text{slope}$
$1/0.01345 = 74.34 \text{ mg}$	$1/0.46752 = 2.139$
$K_L = 1/(q_m \times \text{intercept})$	$K_F = e^{\text{intercept}}$
$1/(74.34 \times 0.47722) = 0.028$	$e^{1.61538} = 5.030$

Table 5
Comparison of Amberlite IRA 743 resin with other resins [39]

Ion-exchange resins	Functional group	Experimental conditions	Adsorption capacity (mmol/g)	Adsorption isotherm
Diaion CRB 02 [40]		pH: 9–9.2 T: 308 K	0.69	
Purolite S108 [41]		pH: 9–9.2 T: 308 K	0.58	
Dowex 2X8 [42]	N-methyl-d-glucamine (NMDG)	pH: 9 T: 298 K	3.4	Langmuir model
Dowex XUS 43594.00 [43,44]		pH: 8.4 T: 298 K	0.31	
This study (Amberlite IRA 743 resin)		pH: 9.4 T: 298 K	6.8	

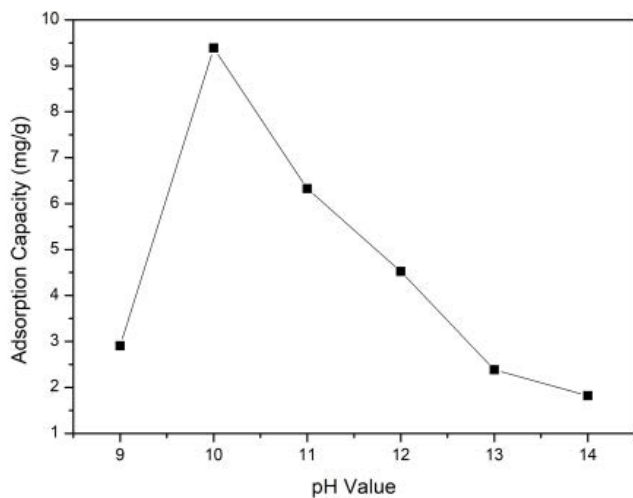


Fig. 5. Effect of initial pH value of boron adsorption.

3.3. Adsorption of boron from desalination brine – effect of liquid–solid ratio (L/S ratio)

The L/S ratios were set up from 100 to 1,000 to investigate the adsorption efficiency in this process. Other fixed parameters were pH 10, contacting time of 1,024 min, and 298 K. Fig. 6 demonstrates that the adsorption capacity of boron was 18.9 mg/g when the L/S ratios were 100, 125, and 200. However, the adsorption capacity would decrease slightly when the L/S ratio increased. (The adsorption capacities were 17.39, 16.38, and 15.83 at the L/S ratio of 250, 500, and 1,000, respectively.) This indicated that adequate Amberlite IRA 743 resin is crucial for adsorbing boron in desalination brine. Although L/S ratios of 100, 125, and 200 could obtain an equal concentration of boron, L/S ratio of 200 was chosen as the optimal parameter in this research to reduce the amount of resin usage.

3.4. Adsorption of boron from desalination brine – effect of contacting period

The contacting periods were set up from 2 to 1,024 min, and other fixed parameters were pH 10, L/S ratio of 200, and 298 K. Fig. 7 illustrates that the reaction rate of boron adsorption through Amberlite IRA 743 resin was not quick. The adsorption capacities slowly increased from 1 min to 16 min. (The adsorption capacities were 8.47, 9.25, 9.83, 10.41, and 11.22 for the adsorptive period of 1, 2, 4, 8 and 16 min, separately.) After that, the adsorption capacity increased dramatically and achieved an equilibrium state from 128 min. (The adsorption capacities were 14.35, 15.21, and 18.9 for the adsorptive period of 32, 64, and after 128 min, respectively.) Therefore, considering recovering the most boron in a limited time, 128 min is the optimal parameter in this procedure.

3.5. Adsorption of boron from desalination brine – thermodynamics

After getting the parameters of the initial pH value, L/S ratio, and contacting period, the thermodynamics of

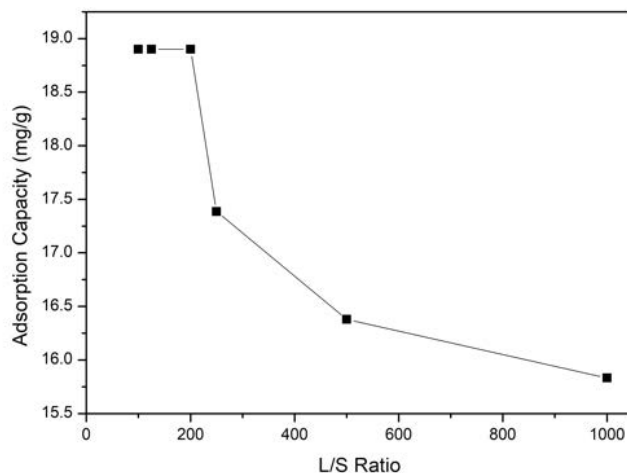


Fig. 6. Effect of L/S ratio of boron adsorption.

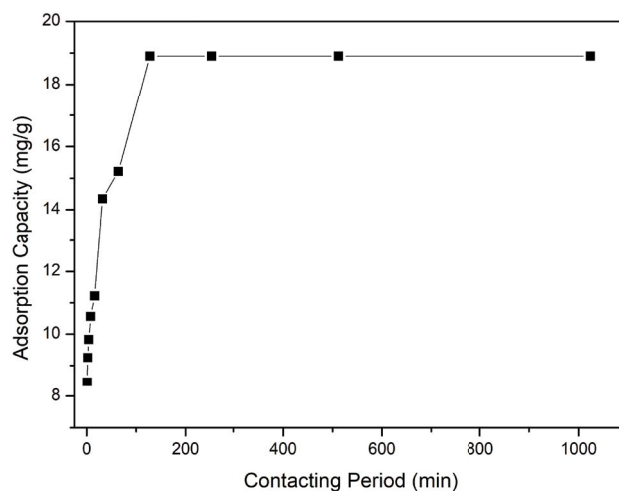


Fig. 7. Effect of contacting period of boron adsorption.

boron adsorption through Amberlite IRA 743 resin was then explored. The temperatures were set up from 288 to 328 K, and the fixed parameters were pH 10, L/S ratio of 200 for 128 min. Fig. 8 reveals that the partition coefficient increased with rising temperature, representing that a higher temperature led to more efficient boron adsorption through Amberlite IRA 743 resin. In accordance with the slope and intercept in Fig. 8, enthalpy, entropy, and Gibbs free energy could be calculated by Eqs. (6)–(10). Table 6 shows that ΔS and ΔH of boron adsorption were positive, demonstrating that the adsorption behavior was conducive at high temperatures, and ΔG_s were all negative under all conditions mean the boron adsorption through Amberlite IRA 743 resin was spontaneous. Because a higher temperature could adsorb much boron, 328 K would be chosen as the operational temperature. To sum up, the optimal parameters were pH 10, L/S ratio of 200, contacting period of 128 min, and 328 K in the adsorption process, and all boron ions could be adsorbed from the desalination brine. Moreover, Amberlite IRA 743 resin could be reused three times in this experiment. After reusing three times, the

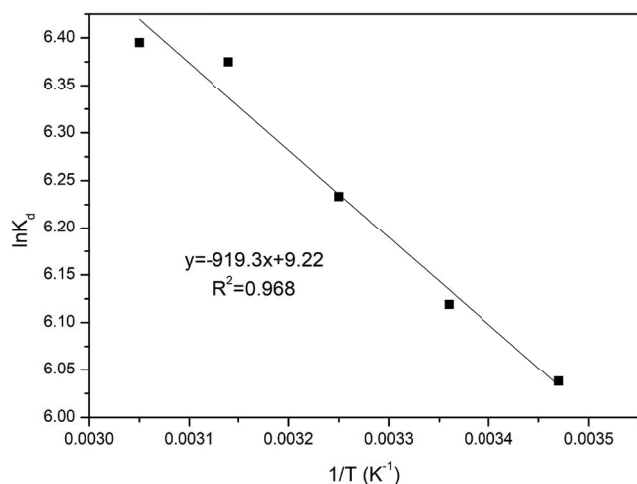


Fig. 8. Partition coefficient ($\ln K_d$) of boron adsorption at different temperatures ($1/T$).

Table 6
Thermodynamic data of boron adsorption through Amberlite IRA 743 resin

K	$\ln K_d$	ΔS (J/mol K)	ΔH (kJ/mol)	ΔG (kJ/mol)
288	6.038			-14.46
298	6.119			-15.16
308	6.233	76.66	7.64	-15.96
318	6.375			-16.85
328	6.395			-17.44

adsorption efficiency of boron would fall below 90%, and the resins needed to be replaced with new ones. (The reason we chose 90% is that we wanted to recover more boron.)

3.6. Desorption of boron from resin – desorbing agent

After adsorbing boron from the desalination brine through Amberlite IRA 743 resin, different agents were tested to desorb boron from the resin to the solutions. The chemicals were sulfuric acid (H_2SO_4), nitric acid (HNO_3), hydrochloric acid (HCl), sodium hydroxide solution (NaOH), ammonia (NH_4OH), and DI water (H_2O). The desorption process was conducted under the conditions of L/S ratio of 200 for 1,024 min at 298 K. Fig. 9 illustrates the desorption efficiencies of all agents in the concentration of 1 M. It can be found that HCl and NH_4OH could not desorb boron from the resin. The desorption efficiencies of HNO_3 , H_2SO_4 , and DI water were 3.8%, 5.1%, and 2.0%, respectively. The only suitable agent in this research was NaOH, and its desorption efficiency was 50.6%. The conjectured reason was that NaOH could release much OH^- which exchanged boron from the resin. Although more boron may be desorbed back under higher NaOH concentrations, 1 M was chosen as the optimal parameter to reduce the usage of chemicals. Furthermore, the pH value of NaOH solution with boron ion would be adjusted to pH 7–10 to acquire borax solutions ($Na_2B_4O_7 \cdot 10H_2O$). By doing this, desorbed boron

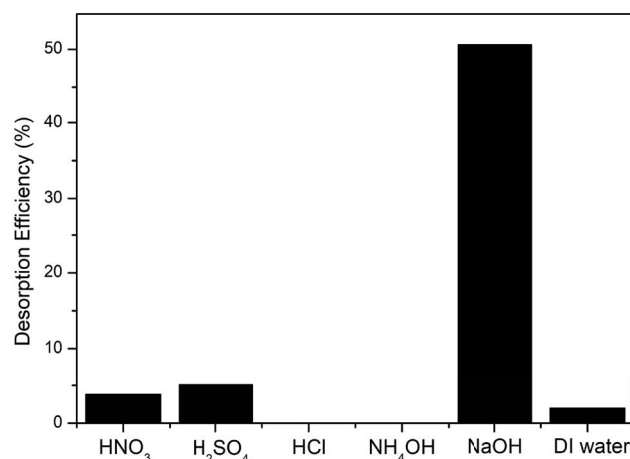


Fig. 9. Desorption efficiencies of boron through different agents.

from the desorbed solution could be recovered. Solid borax would then be acquired by vacuum drying and applied in other industries to reach the goal of resources circulation.

4. Conclusion

This research applied an Amberlite IRA 743 batch system to recover boron from the desalination brine. The results reveal that the saturated adsorption capacity of boron through Amberlite IRA 743 resin was 74.34 mg/g and conformed to the Langmuir model. In the adsorption procedure, 18.9 mg/L of boron could be fully adsorbed from brine through the resin under the conditions of pH 10, L/S ratio of 200, contacting period of 128 min, and temperature at 328 K. Besides, this adsorption reaction was spontaneous under all conditions and was efficient at a higher temperature. After adsorbing process, boron could be desorbed by 1 M of sodium hydroxide solutions, and solid borax could be acquired by vacuum drying the solutions. To sum up, the boron adsorption through Amberlite IRA 743 system is a promising method with low environmental impact, low-cost, and low energy consumption. If the desorption efficiency could be ameliorated in the future, it would be an efficient technique to recover boron resources from desalination brine and towards a circular economy.

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