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Optimal conditions for recovering boron from seawater using boron selective resins

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Abstract−We determined the optimal conditions for efficient recovery of boron from seawater using boron selective resins (BSRs). A commercialized BSR named CRB05 was adopted and prepared in two particle sizes: A fine-particulate BSR (effective particle size of 105 μm) and a coarse-particulate BSR (effective particle size of 445 μm). The performance of the two BSRs was compared in terms of boron adsorption, boron desorption, and BSR regeneration and reusability. During boron adsorption, for fine BSR, optimal reaction time, stirring speed and the amount of BSR needed for the adsorption of boron were 30 min, 150 rpm and 1 g-BSR/L respectively, whereas for coarse BSR, values of the above parameters were 300 min, 150 rpm and 3 g-BSR/L. It indicates that the fine BSR can adsorb boron about three-times more than the coarse BSR. It also shows that the reaction rate of the fine BSR is almost ten-times higher than that of the coarse BSR. During the boron desorption, no significant difference was found between the efficiencies exhibited by the fine and the coarse BSRs. The best desorption performance can be attained with 11.9 mL/mg-B of 0.05 M H_2SO_4 and 15.9 mL/mg-B of 0.25 M HCl, regardless of the particle size of the BSR. Finally, the boron adsorption efficiency can be maintained at a stable level even after reusing the BSRs over ten times. The present study shows a possibility to recover boron with better efficiency from seawater in short time using the fine BSR, rather than the coarse BSR.

Keywords: Boron, Seawater, Boron Selective Resin (BSR), Recovery, Particle Size

INTRODUCTION

Boron, B, is a metalloid which belongs to Group 13 in the periodic table and exists in the forms of both boric acid, $B(OH)_3$, and borate ion, $B(OH)_4^-$, in water as shown below:

$$B(OH)_3+H_2O \leftrightarrow B(OH)_4^-+H^+ \qquad pK_a=9.2 \text{ at } 25\,^{\circ}C$$

In seawater, particularly, boron exists mostly in the form of $B(OH)_3$, which is slightly alkaline (pH 7.5-8.5). The concentration of dissolved boron in seawater is very low, which is about 4.5 mg/L. Nevertheless, it is estimated that approximately 5.4 billion tons of boron is dissolved in all of the seawater on earth, corresponding to about 7,000 times more than the boron resources on land.

Boron is essential for various industries, including the glass industry, semi-conductor industry, nuclear power plant, and medical industry. In recent years, the use value of the boron has been soaring with the development of new technology. At the present time, however, the worldwide mining of boron is estimated to last for only 42 years from now on [1], and the mining environment on land is consistently deteriorating because the purity of boron decreases and the mining cost increases. Therefore, we believe that it is very urgent to develop new technology to recover boron from seawater. Even though many studies have been actively conducted so far to recover lithium, uranium, and other resources from seawater, there is barely any effort put into studying how to recover boron from seawater.

Most of the studies related to boron treatment conducted so far have focused on removing boron from seawater during the desalination process [2-7]. Only a small number of studies, on the other hand, have been carried out for the purpose of recovering boron from geothermal wastewater, salt lakes, and industrial wastewater with relatively high concentration of boron [2,8-13]. Although a few researches are found on the artificial seawater in literature [5], there is little study on using the actual seawater to recover boron.

Table 1 shows the structures, particle sizes, and adsorption capacities of boron selective resins (BSRs) that are commercially available in the USA, Japan and UK. These BSRs contain N-methyl-glucamine (NMG) group (Fig. 1) and are known to be superior to other boron adsorbents in terms of the boron selectivity and the adsorption capacity [14]. As shown in Table 1, the commercially available BSRs are composed of at least 300 μm of particles, implying that the particles are large enough to be usually loaded in columns.

The adsorption capacity of currently available BSRs is about 0.7-1.2 eq/L. These values are not high enough to efficiently recover boron from seawater because the concentration of boron in seawater is very low. So far, only a few researches have been conducted to improve the adsorption capacity of BSR by reducing the particle size below 100 μm while recovering boron from either geothermal wastewater [9,13] or artificial seawater [5]. No study, however, is found in literature to recover boron from the actual seawater.

In the present study, we prepared a commercially available BSR, named CRB05, in two particle sizes: a fine-particulate BSR (fine BSR) and a coarse-particulate BSR (coarse BSR). Then they were used to derive the optimal conditions for efficiently recovering boron from (the actual) seawater by making experiments on the boron adsorption, the boron desorption and the BSR reuse in sequence. The performance of the two BSRs was compared with each other.

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Table 1. Commercially available boron selective resins [15]

Country company	Product	Polymer structure	Functional group	Mean diameter (μm)	Total capacity (eq/L)
USA	AmberliteTM PWA10	Macroporous polystyrene	N-Methylglucamine	300-1200	≥0.7
Rohm & Haas	AmberliteTM IRA743	Macroporous polystyrene	N-Methylglucamine	500-700	≥0.7
Japan	Diaion CRB01	Macroporous polystyrene-DVB	N-Methylglucamine	300-1200	≥1.2
Mitsubishi	Diaion CRB02	Macroporous polystyrene-DVB	N-Methylglucamine	300-1200	≥0.9
Chemical Co.	Diaion CRB03	Macroporous polystyrene-DVB	N-Methylglucamine	350-550	≥0.7
	Diaion CRB05	Macroporous polystyrene-DVB	N-Methylglucamine	350-850	≥0.95
USA	DowexTM BSR-1	Macroporous polystyrene-DVB	N-Methylglucamine	550±50	≥0.7
Dow Chemical					
UK	Purolite S108	Macroporous polystyrene-DVB	N-Methylglucamine	650±70	≥0.6
Purilite Interna. Co.	Purolite S110	Macroporous polystyrene-DVB	N-Methylglucamine	600±100	≥0.8

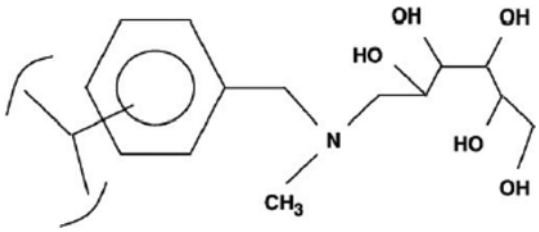

Fig. 1. The structure of boron selective resin containing NMG group [16].

Our aim is to present the possibility for efficiently recovering boron from seawater by determining the optimal conditions for enhancing the recovery efficiency and reducing the reaction time.

MATERIALS AND METHODS

1. Analysis of Materials

The seawater sample was collected from the coast of Korea Maritime and Ocean University located in Busan, Korea and the suspended solids were removed by an 1 μm membrane filter. Then, the concentrations of major dissolved components in seawater were measured using IC, AAS, and UV/Vis spectrophotometer. We used a commercial BSR named CRB05 (Mitsubishi, Japan), which was recently developed to adsorb boron from wastewater with high boron concentration and has quite high boron adsorption capacity (≥0.95 eq/L). The BSR was selected because the concentrations of dissolved components in seawater are quite high like the wastewater and, in addition, it has been barely used by other researchers in previous studies. To examine the effect of the BSR particle size on the boron adsorption, boron desorption, and BSR reuse, two different particle sizes of BSRs were prepared, a fine BSR (the effective diameter of 105 μm) and a coarse BSR (the effective diameter of 445 μm). The fine BSR was made by grinding CRB05 with a mixer mill, whereas the coarse BSR was just an unaltered form of CRB05. The particle size of each BSR was determined using a laser scattering particle size analyzer. The boron concentration was measured by an Azomethine-H method, which is known to be the most convenient and relatively accurate among many methods to measure the boron concentration [17].

2. Boron Adsorption

We performed experiments with both fine and coarse BSRs to find the optimal reaction time, stirring speed, and BSR amount required during the adsorption of boron from seawater according to the following basic procedure:

(1) 100 mL of seawater and 0.5 g of each BSR are put together into a 250 mL Erlenmeyer flask and then the mixture is stirred in a shaking incubator at a speed of 150 rpm (25 °C).

(2) The flask is taken at the designated reaction time after the start, which is set at 30 minutes for the fine BSR and at 300 minutes for the coarse BSR.

(3) Each BSR is filtered using a 0.45 μm membrane filter and then the concentration of boron remaining in the filtrate (C_e) is measured using an UV/Vis spectrophotometer.

(4) The boron adsorption efficiency of each BSR is attained by calculating the difference in the boron concentration before (C_0) and after (C_e) the adsorption reaction. (Boron adsorption efficiency (%)= $(C_0-C_e/C_0)\times100$

To determine the optimal value of each parameter, we repeated the same experiments by varying only the parameter at pre-designated values while following the basic procedure mentioned above. The reaction time was pre-designated at 15, 30, 90, 180, 240, 300, and 360 minutes, while the stirring speed was designated at 0, 50, 100, 150, 200, 250, and 300 rpm. The BSR amount, on the other hand, was varied at 0.02, 0.05, 0.1, 0.2, 0.3, 0.4, and 0.5 g. Note that the values of the parameters, such as 30 and 300 minutes, and 150 rpm, used in the basic procedure were determined as the optimal conditions from the previous experiments. The BSR amount, 0.5 g, was also determined to be quite sufficient to adsorb all of the boron from 100 mL of seawater.

3. Boron Desorption

We attempted to desorb boron from the saturated BSRs obtained through the boron adsorption process using two kinds of acids, H_2SO_4 and HCl. We performed experiments to find the optimal concentration and volume of each acid required during the boron desorption. Note that the boron amounts adsorbed in the saturated fine and coarse BSRs were measured to be 4.2 mg-B/g-BSR and 1.4 mg-B/g-BSR, respectively. Here, the volume of acid was defined as the volume of acid (mL) required for desorbing each milligram of the adsorbed boron. The basic procedure for the experiments

was as follows:

(1) Each of the two acid solutions, 0.05 M of H_2SO_4 and 0.25 M of HCl, were mixed with the saturated BSR at a fixed mixing ratio, that is, 50 mL/g-BSR for the fine BSR and 16.7 mL/g-BSR for the coarse BSR (both corresponding to 11.9 mL/mg-B). Here, the mixing ratio was selected on the basis of the minimum volume of the acid required to fully immerse the saturated BSR. Subsequently, the mixture was left to remain as it was for 24 hours.

(2) After the desorption reaction was complete, the BSR was filtered with a 0.45 μm membrane filter and then the boron concentration of the filtrate was measured by using a UV/Vis spectrophotometer.

(3) The boron desorption efficiency was calculated with the amount of boron adsorbed by the saturated BSR (C_0) and the boron concentration of the filtrate (C_e) after the desorption reaction. (Boron desorption efficiency (%)=(C_e/C_0)×100)

To determine the optimal acid concentration, we repeated the same experiments by varying the concentration at 0.02, 0.05, 0.1, 0.25, 0.5, 1, and 2 M. For the optimal acid volume, on the other hand, we varied the mixing ratio at 3.3, 16.7, 33.3, 50, 66.7, and 83.3 mL/g-BSR for the fine BSR and at 1.1, 5.6, 11.1, 16.7, 22.2, and 27.8 mL/g-BSR for the coarse BSR. The volume of acid used for saturated fine BSR was three-times more than that for saturated coarse BSR because unit mass of saturated fine BSR contains three-times more boron compared to that of saturated coarse BSR. Note that the mixing ratios correspond to 0.79, 4.0, 7.9, 11.9, 15.9, and 19.8 mL/mg-B, respectively, for both BSRs.

4. Regeneration and Reuse of BSR

We performed experiments using NaOH to see if the BSRs used once or more can be regenerated or reused, according to the following basic procedure:

(1) Each of the fine and coarse BSRs, which had already gone through the boron adsorption and desorption reactions once, was mixed with 0.25 M NaOH at a fixed mixing ratio, that is, 50 mL/g-BSR for the fine BSR and 16.7 mL/g-BSR for the coarse BSR. Next, the mixture was left to remain as it was for 24 hours.

(2) After the regenerated BSR was washed with distilled water, the adsorption experiment (see section *Boron Adsorption*) was performed to compare the boron adsorption efficiency of the BSR before and after the regeneration.

(3) The processes composed of the boron adsorption, boron desorption and BSR regeneration were repeated ten times using the same BSR to verify the long-term reusability.

RESULTS AND DISCUSSION

1. Analysis of Materials

Table 2 shows the concentrations of major dissolved components in seawater. It is confirmed that the compositions of the seawater samples used in the present study are in good agreement with those of the references. The boron concentrations in the samples vary with time between 4.3 mg/L and 4.6 mg/L, which yields 4.43 mg/L of the concentration on average. The pHs of the samples range 7.8-8.4, implying that they are slightly alkaline. Table 3 shows the physical and chemical properties of the commercial BSR named CRB05 used in the present study. The coarse BSR has an effective diameter of 445 μm (300-850 μm) and the adsorption capacity of 1.10 eq/L (16.47 mg-B/g-BSR). The fine BSR, on the other hand, has an effective diameter of 105 μm (10-300 μm).

Table 3. Physical and chemical properties of CRB05

Parameter	Unit	Value
Whole bead content	%	98
Acid exchange capacity	eq/L	1.10
Moisture content (R-OH)	%	47.0
Shipping density (R-OH)	wet-g/wet-L	722
Swelling rate (R-OH)	wet-mL/dry-g	2.6
Average diameter	μm	541
Effective diameter	μm	445
Uniformity coefficient		1.27

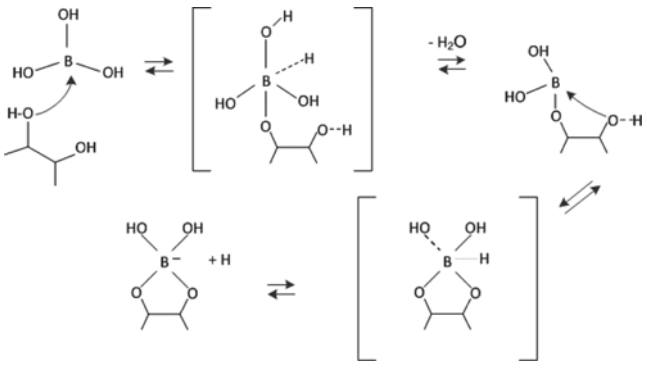

Fig. 2. Binding mechanism of boron by NMG type resin [16].

2. Boron Adsorption

The BSR, CRB05, used in the present study contains the NMG group, as shown in Fig. 1. The group seizes boron due to the tendency to be covalently bonded with the boric acid and then forms a complex, as shown in Fig. 2 [14,16,19]. The tertiary amine in the NMG group particularly plays a very important role in capturing hydrogen ions produced during the process of forming a borate ester complex.

2-1. Reaction Time

Fig. 3 shows the effect of the reaction time on the boron adsorp-

Table 2. Chemical compositions of seawater

Seawater	Concentration (mg/L)							
	B	Cl	Na	Mg	S	Ca	K	Br
This study	**4.43**	19,194	11,280	1,360	856	428	365	52
Wright and Colling [18]	**4.40**	19,500	10,770	1,290	905	412	380	67

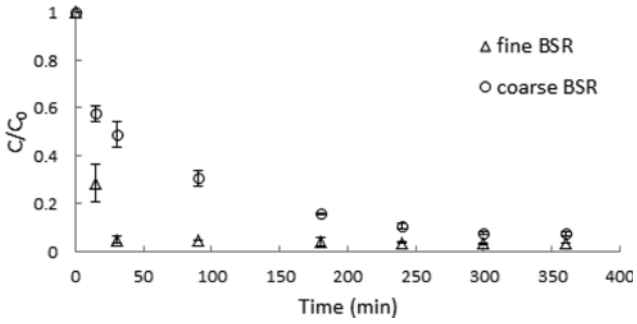

Fig. 3. Adsorption efficiency of boron according to the reaction time.

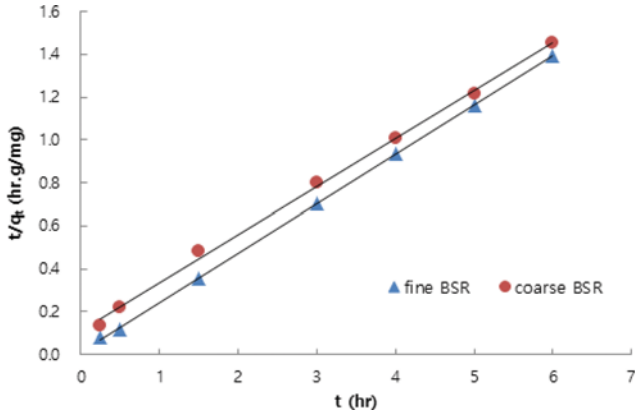

Fig. 4. Plots of linear fitting on the data obtained by applying the pseudo-second order model to the adsorption of boron onto BSR.

tion for both fine and coarse BSRs. The reaction for the fine BSR is ten-times faster than that for the coarse BSR. That is, the boron adsorption reaction reaches a steady state after 30 minutes for the former case, whereas it reaches after 300 minutes for the latter case. It seems to be because the fine BSR has larger surface area for providing more room required while reacting with boron than the coarse BSR. The boron in seawater, $B(OH)_3$, therefore, is more likely to arrive at the surface of BSR [14].

The kinetics data are described using five adsorption kinetic models, including pseudo-first order, pseudo-second order, Elovich, power function, and intra-particle diffusion models (see Table 4). For the adsorption of coarse BSR, the pseudo-second order, Elovich, and power function models yield R^2>0.99, and thus show better correlation with the experimental data than the pseudo-first order (0.9307) and intra-particle diffusion (0.9075) models. For that of fine BSR, on the other hand, the pseudo-second order model provides R^2 of 0.9999, and thus exhibits the best fit with the experimental data. The plots of linear fitting on the data obtained for the pseudo-second order model are shown in Fig. 4.

Several researchers conducted boron adsorption experiments using commercialized BSRs, XUS 43594 and CRB02, in two particle sizes (45-75 μm and 355-500 μm) on the artificial seawater and obtained results similar to those of the present study [3,9]. Their results showed that the BSR with smaller particles reacts much faster than the other. In addition, they reported that, when the BSR particle sizes are large (355-500 μm), the reaction rates of XUS 43594 and CRB02 are different from each other. When the particle sizes are small (45-75 μm), however, they are nearly the same. Santander et al. [13], on the other hand, recently performed boron adsorption experiments on geothermal water by using two kinds of BSRs in each two particle sizes: synthesized BSR with 100-180 μm and 180-250 μm and CRB02 with 250-355 μm and 355-500 μm. The results showed that the reaction time for reaching the steady state is not changed so much by small change of the particle size. On basis of the results, they concluded that there is virtually difference in the boron adsorption rate only when the particle sizes are significantly different from each other. Our experimental results show that the boron adsorption rate extremely increases when the particle size of BSR is significantly reduced.

2-2. Stirring Speed

As shown in Fig. 5, the boron adsorption efficiency is very low when the stirring speed is under 50 rpm for both fine and coarse BSRs. Then the efficiency increases with the stirring speed until the speed reaches a certain value, 100 rpm for the fine BSR and 150 rpm for the coarse BSR, and finally it becomes constant. It is believed

Table 4. Kinetic parameters regarding the adsorption of boron onto BSR

Kinetic equation	Equation	Linear plot	Correlation		R^2	
			f-BSR	c-BSR	f-BSR	c-BSR
Pseudo-first order	$q_t = q_e(1-e^{-k_1 t})$	$\ln(q_e-q_t)$ vs t	$\ln(q_e-q_t) = -1.2173t - 0.2088$	$\ln(q_e-q_t) = -0.9832t + 1.3605$	0.7084	0.9307
Pseudo-second order	$\frac{t}{q_t} = \frac{1}{k_2 q_e^2} + \frac{t}{q_e}$	$\frac{t}{q_t}$ vs t	$\frac{t}{q_t} = 0.2302t + 0.0108$	$\frac{t}{q_t} = 0.2245t + 0.1097$	0.9999	0.9979
Elovich	$q_t = \frac{1}{b}\ln(ab) + \frac{1}{b}\ln(t)$	q_t vs ln(t)	$q_t = 0.2594\ln(t) + 3.9639$	$q_t = 0.7511\ln(t) + 2.8649$	0.5730	0.9934
Power function	$\ln\left(\frac{q_t}{q_e}\right) = A \times \ln(t) + B$	$\ln\left(\frac{q_t}{q_e}\right)$ vs ln(t)	$\ln\left(\frac{q_t}{q_e}\right) = 0.0696\ln(t) - 0.09$	$\ln\left(\frac{q_t}{q_e}\right) = 0.2569\ln(t) - 0.4113$	0.5652	0.9923
Intra-particle diffusion	$q_t = k_{ip} t^{0.5} + a_{ip}$	q_t vs $t^{0.5}$	$q_t = 1.2355t^{0.5} + 1.9294$	$q_t = 1.5531t^{0.5} + 0.7959$	0.5313	0.9075

q_e, equilibrium capacity; q_t, capacity at t; t, adsorption time; k_1, adsorption rate constant; k_2, adsorption rate constant; a, b, Elovich constants; A, B, power function constant; k_{ip}, diffusion rate constant; a_{ip}, indicates thickness of the boundary layer

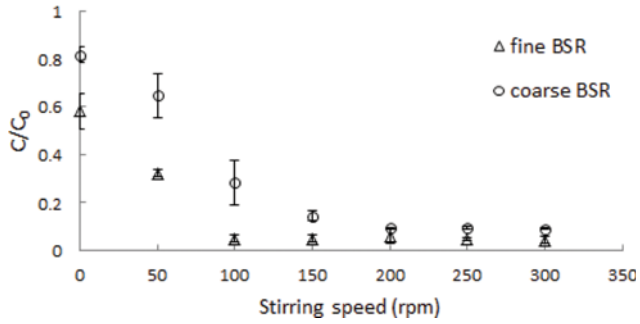

Fig. 5. Adsorption efficiency of boron according to the stirring speed.

that when the seawater is stationary, the BSR piles up on the bottom, thus decreasing the contact probability between the BSR and the seawater. To effectively adsorb boron, therefore, water should flow well so that the BSR can come in sufficient contact with the seawater. Fig. 5 indicates that the optimal stirring speed for the fine BSR is lower than that for the coarse BSR. It is because the fine BSR weighs less than the coarse BSR and thus can come into smoother contact with the seawater even for the lower stirring speed.

Previous studies reported that the boron adsorption efficiency is not affected so much by the stirring speed when the speed is relatively high, for example, as much as 100-750 rpm [6] or 350-750 rpm [8]. In the present study, however, adsorption experiments were performed at a relatively low stirring speed ranging 0-350 rpm to simulate the movement of water in the ocean. The present results, therefore, can be used as basic data for determining the optimal water flow according to the BSR particle size for the boron recovery from seawater. It is determined that 150 rpm is the optimal stirring speed for both fine and coarse BSRs.

2-3. Amount of BSR

As shown in Fig. 6, the adsorbed boron gets more as the amount of BSR increases up to a certain value, i.e., 0.1 g/100 mL for the fine BSR and 0.3 g/100 mL for the coarse BSR. Afterwards, it becomes constant, resulting in the same boron adsorption efficiency of 95% for both BSRs. The optimal amounts are found to be 1 g/L and 3 g/L for the fine and coarse BSRs, respectively, which can be explained by the difference in the particle size. The fine BSR can adsorb boron more effectively than the coarse BSR because the smaller particle size increases the surface area and also the diffusion rate of boron [3]. These results indicate that high boron adsorption efficiency can be obtained even with a very small amount of BSR if the

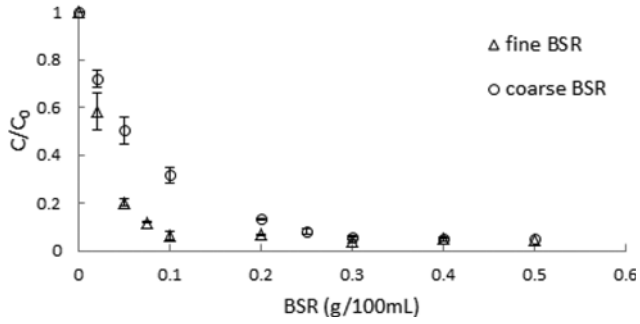

Fig. 6. Adsorption efficiency of boron according to the BSR amount.

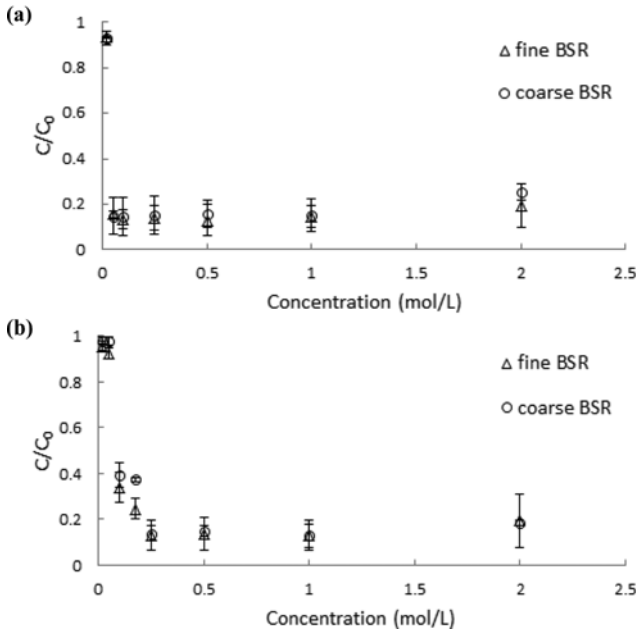

Fig. 7. Desorption efficiency of boron from BSR according to the acid concentration: (a) H_2SO_4 (b) HCl.

size of BSR becomes small, corresponding to a few tens of micrometers. Thus, it is implied that boron can be effectively recovered even from seawater with low boron concentration in the future.

3. Boron Desorption

We performed experiments on the boron desorption and found that the optimal concentrations and volumes of the acids exhibit similar results between both fine and coarse BSRs (see Figs. 6 and 7). Thus, there is virtually little correlation between the BSR particle size and the boron desorption efficiency.

3-1. Concentration of Acid

As shown in Fig. 7, the boron desorption efficiency displays the highest value, 85±5%, at 0.05 M for H_2SO_4, while it displays the highest one, 87±5%, at 0.25 M for HCl. In addition, the desorption efficiency does not always increase even with increase in the acid concentration. For example, the efficiency actually decreases while the concentration of each acid reaches 2 M. This means that since the hydrogen ion concentration makes a significant effect on the boron desorption, we need to be able to control the concentration of acid in order to effectively desorb boron from the BSR.

Kabay et al. investigated the desorption performance of H_2SO_4 and HCl according to their concentrations using BSRs such as CRB01 and S108 and then reported that 0.5 M H_2SO_4 and 1 M HCl are the most efficient in the boron desorption [2]. As the concentration of H_2SO_4 increased from 0.05 M to 0.5 M, there was no difference in the boron desorption efficiency. In addition, HCl also showed similar characteristics of the desorption efficiency in the concentration range of 0.1-1.0 M. As the concentrations of the acids were low, however, the desorption reaction took very long. Parschova et al. [4], on the other hand, reported that the desorption efficiency increases with increasing concentration of HCl between 0.1 M and 0.5 M, but the efficiency at 1 M HCl is lower than that at 0.5 M.

Since the hydrolysis reaction to desorb boron from BSR usually

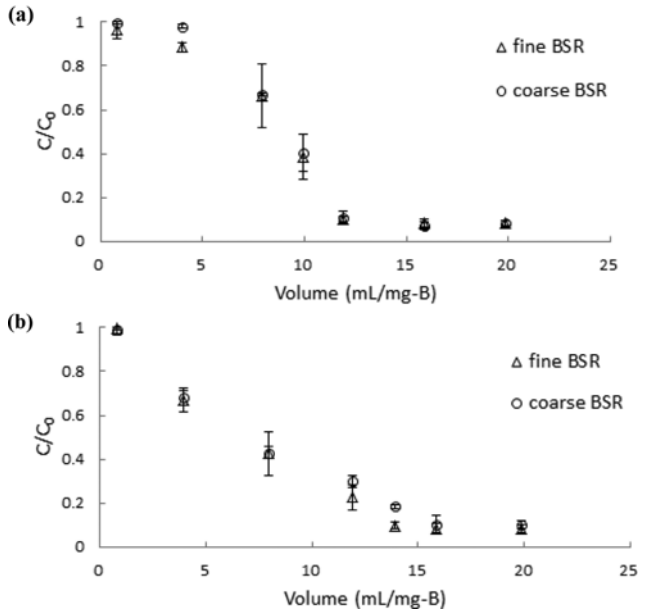

Fig. 8. Desorption efficiency of boron from BSR according to the acid volume: (a) 0.05 M H_2SO_4 (b) 0.25 M HCl.

occurs below pH 1, boron can be effectively and quickly desorbed if an acid with appropriate concentration is used [16,19]. According to Marston et al. [16], even more acid is required than the amount determined by the stoichiometry during the boron desorption reaction because the NMG group is linked with styrene matrix through the tertiary amine group which captures hydrogen ions as shown in Fig. 1.

3-2. Volume of Acid

Fig. 8 shows how the boron desorption efficiency varies with the volume of each of the acids, 0.05 M H_2SO_4 and 0.25 M HCl. It is observed that the desorption efficiency increases until the volume reaches a certain value, that is, 11.9 mL/mg-B for 0.05 M H_2SO_4 and 15.9 mL/mg-B for 0.25 M HCl, and afterwards does not change. The boron desorption efficiencies were measured to be 89±2% and 91±3% at the optimal volumes of 0.05 M H_2SO_4 and 0.25 M HCl, respectively, and there is no significant difference between them.

The boron desorption reaction by the acid will proceed in the reverse order of the adsorption reaction shown in Fig. 2, and it will be accelerated if a large amount of hydrogen ions are supplied. According to the stoichiometry, the molar ratio between the boron to desorb and the required hydrogen ion is 1 : 1. In this study, 11.9 mL of 0.05 M H_2SO_4 or 15.9 mL of 0.25 M HCl was required to desorb 1 mg of boron from the saturated BSR. The amounts are 6.4 and 42.9 times more than those calculated by the stoichiometry for H_2SO_4 and HCl, respectively. The optimal concentrations and volumes of the acids obtained in the present study are not only necessary to reduce the cost, but also to increase the boron concentration in the desorption solution.

4. Regeneration and Reuse of BSR

We continued to perform experiments on the BSR reuse in seawater by repeatedly regenerating the BSRs. It was found that the fine and coarse BSRs which were reused ten times could still yield boron adsorption efficiencies as much as 90±5% and 92±3%, respectively (Fig. 9). These results indicate that the BSRs can be both used semi-permanently for adsorbing boron from seawater. It is also implied that boron can be effectively recovered from seawater by undergoing the processes of boron adsorption, boron desorption and BSR regeneration under the optimal conditions determined in this study. Meanwhile, the adsorption efficiency of the reused fine BSR slightly decreases with increasing number of the repetitive experiments because the particles are liable to be lost due to their small size.

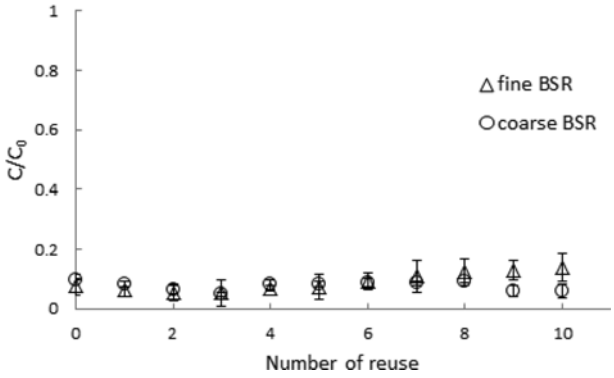

Fig. 9. Adsorption efficiencies of boron by BSRs that were already 10 times used.

To recover boron from geothermal wastewater (20-30 B-mg/L), Kabay et al. [2] used CRB02 for boron adsorption, 5% H_2SO_4 for the boron desorption, and 4% NaOH for the BSR regeneration in sequence. As a result, they could reuse the BSR ten times with little deterioration of the adsorption efficiency. In addition, Nadav [20] reported that the boron adsorption efficiency of the reused BSR can be even more improved through the sequential process such as treatment with H_2SO_4 and neutralization with NaOH than the single process only with H_2SO_4. They also explained that the performance of the reused BSR after the neutralization with base can be slightly improved compared to that of the first use because the base improves the function of BSR surface uniformly throughout.

Kose and Ozturk [21] used a strong basic anion resin, Dowex2×8, to conduct boron removal experiments and found that the boron adsorption efficiency at the second and third uses of BSR after the treatment such as boron desorption with acid and regeneration with base is slightly higher than that at the first use without any treatment. The results in our study are similar to theirs. It is suggested that the purchased BSR should be treated with acid and base before using them to obtain more accurate results.

As known through the boron adsorption mechanism shown in Fig. 2, it is theoretically possible to regenerate the hydroxyl group (-OH) of NMG at the BSR surface through the boron desorption using the acid alone, and the primary purpose for using base is neutralization [22]. In other words, the optimal condition of the base is less important than that of the acid since the base is only used for neutralization.

CONCLUSIONS

We performed experiments following boron adsorption, boron

desorption, and BSR regeneration in sequence to investigate the optimal conditions for efficiently recovering boron from seawater using BSRs. A commercialized BSR named CRB05 was prepared in two different particle sizes: a fine-particulate BSR (effective diameter of 105 μm) and a coarse-particulate BSR (effective diameter of 445 μm). The results obtained were as follows:

(1) For the effective boron adsorption from seawater, the optimal reaction time, stirring speed, and amount of BSR depend strongly on the particle size of BSR. We obtained the best performance at 30 minutes, 150 rpm and 1 g-BSR/L for the fine BSR, and at 300 minutes, 150 rpm and 3 g-BSR/L for the coarse BSR. That is, the reaction for the fine BSR is ten-times faster than that for the coarse BSR, and the required amount for the fine BSR is one-third of the amount of coarse BSR.

(2) There is virtually no variation in the boron desorption efficiencies with the particle size. The optimal concentrations and volumes of acid for the boron desorption are, respectively, 0.05 M and 11.9 mL/mg-B for H_2SO_4, and 0.25 M and 15.9 mL/mg-B for HCl.

(3) Both BSRs of different particle sizes can be reused more than ten times with little deterioration of their adsorption efficiencies by desorbing boron with acid from the used BSRs, and then neutralizing them with 0.25 M NaOH.

It is very difficult to recover boron from seawater since the boron concentration in seawater is low and bio-fouling often occurs on the BSR surface. This study, however, shows that boron can be recovered from seawater efficiently when the adsorption performance is significantly improved and the reaction time is shortened by using the fine BSR.

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