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Removal of boron by boron-selective adsorbent prepared using radiation induced grafting technique

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ABSTRACT

Boron-selective adsorbent was synthesized by grafting the glycidyl methacrylate onto polyethylene (PE) non-woven fiber using electron beam ionizing radiation. Subsequently, the grafted PE with 180% degree of grafting was chemically modified using n-methyl-d-glucamine (NMDG). The density of NMDG of the synthesized adsorbent was 2.2 mmol/g. Batch mode adsorption's test showed that pH ranging from 4 to 8 had highest adsorption capacity and the adsorption capacity of the grafted adsorbent was 14.5 mg-B/g-adsorbent. Column mode adsorption test showed a marginal reduction of total breakthrough capacity from 13.8 to 12.7 mg-B/g-adsorbent, for feeding speed of space velocity (SV) 15 and SV 400, respectively. This indicated that the synthesized adsorbent had exhibited high performances of boron adsorption and desorption process. High performances of the prepared adsorbent could contribute from few factors such as fine size of the adsorbent, large surface area, and homogeneous pore size. Desorption of boron using 1 M HCl was completed at bed volume of 10. It showed that, the effect of feeding flow between SV 15 and SV 400 to the desorption process was negligible. Thus, the prepared adsorbent could be operated in high feeding speed and pressure. This would significantly improve the cost of the treatment.

Keywords: Adsorption; Boron; Desorption; Glucamine; Radiation graft polymerization

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1. Introduction

Boron is distributed in the environment as a result of both natural sources and anthropogenic activities. Although boron is regarded as micronutrient for living organisms, the range between deficiency and excess is narrow. WHO and EU have recommended a limit of 2.4 mg/l [1] and 0.5 mg/l, respectively, for drinking water. Depending on the geological background where fresh water is found, the content of boron can be high, exceeding the limit of 1 mg/l. The anthropogenic activity also contributed significantly to the high concentration of boron in surface water.

Many methods have been introduced for boron removal. Removal of boron using resin as adsorbents is the preferable method. The retention order of anions on resin is as follows: $SO_4^{2-} > NO_3^- > PO_4^{3-} > Cl^- > B(OH)_4^-$. Boron has the lowest retention order and this is due to the low affinity of boron. Hence, boron-selective resin is required for effectively

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removing boron found in water to below 1 mg/l. Resin with n-methyl-d-glucamine (NMDG) is the most efficient method or material to remove boron [2]. Other studies reported that using NMDG type resins included boron removal from geothermal water [3,4] and boron removal from seawater [5–7]. Although boron-selective resin is effective in selectively removing the boron found in low and medium ranges of concentration, the performance of boron-selective resin is low in terms of feeding speed. The typical flow rate applied for resin packed in column for boron removal is below 50 space velocity (SV) (h^{-1}). Granular resin has typical diameter of about 0.5 mm [8]. At SV higher than 50 h^{-1}, it has resulted loss of most of the applied pressure. To address the above weaknesses, we use fine non-woven polyethylene (PE) fiber with diameter of about 13 μm to synthesize the adsorbent using radiation grafting technique.

The aim of this study is to synthesize adsorbent that is capable to remove boron selectively at very high flow rates. With substantial improvement on flow rate of feeding water received by the column packed with adsorbent, the size of the entire column devices and cost can be remarkably improved. This technique utilizes radiation to create an active radical in the polymer backbone and follow by monomer being grafted on the active radical. Subsequently, functional groups, NMDG, are introduced to the monomer grafted on polymer backbone. NMDG functional group has high selective affinity to boron. After boron-selective adsorbent was synthesized, batch and column adsorption evaluations were conducted to investigate its performance.

2. Methodology

2.1. Preparation of adsorbent

The preparation of adsorbent would be explained in two steps as follows:

2.1.1. Radiation grafting of fiber

PE non-woven polymer was used as sample to prepare the adsorbent. Nitrogen gas was used to remove the air in the bags after samples had been packed into PE zipped bags. Subsequently, the samples were irradiated with adsorbed dose of up to 100 kGy and used immediately for the grafting of glycidyl methacrylate (GMA). The irradiated samples were transferred to the monomer solution of GMA-1-butanol. The concentration of GMA used in this study was 5% (wt) and 10% (wt). The reaction time ranging from 1 to 4 h and reaction temperature of 40℃ were selected in this study. The degree of grafting (Dg in %) was defined as:

$$\mathrm{Dg}\,(\%) = 100\,(W_1 - W_0)/W_0 \tag{1}$$

where W_0 and W_1 are the weights of sample before and after graft polymerization, respectively.

2.1.2. Introduction of NMDG to the grafted samples

The grafted sample was immersed in NMDG solution. The NMDG solution was prepared using 1–4 dioxane with the weight of NMDG at 10% (wt). The reaction temperature and reaction time were 80℃ and 1 h, respectively. The density of glucamine group was estimated by measuring the increase of weight after chemical modification.

2.2. Batch-mode adsorption of boron

The pH of boron solution for batch mode test was adjusted from 2 to 11 using hydrochloric acid and ammonia solution. Adsorbents were cut into 1 cm × 1 cm unit and placed in 50 ml of boron solution with the concentration of 10 mg/l. The adsorbent was immersed in boron solution for 2 h under rapid stirred condition. After 2 h, the adsorbent was removed and the remaining boron was measured using inductively coupled plasma—optical emission spectroscopy (ICP-OES, Perking Elmer). Removal of boron in mg-B/g-dry of adsorbent was calculated by the equation as follows:

$$\text{Boron removed (mg-B/g-adsorbent)} = [(C_0 - C_1)\,(V/W_{\mathrm{ads}})] \tag{2}$$

where C_0 and C_1 were the initial and equilibrium concentrations of boron; V was the volume of tested solution; and W_{ads} was the weight of the adsorbent.

2.3. Column-mode adsorption of boron

The adsorption of boron in column mode was measured by transferring the boron solution with concentration of 10 mg/l into the column. The pH of the boron solution was adjusted to 6.0 for column mode test. The inner diameter of the column was 10 mm. The amount of adsorbent with diameter of 10 mm packed in the column was 0.45 g. The flow rate as indicated by the SV (h^{-1}) was calculated by dividing the flow rate of boron solution with the volume of adsorbent packed in the column (bed volume). The flow rate of the boron solution transferred to the column was adjusted by the peristaltic pump. The effluent from column was collected using fraction collector. The breakthrough point of 5% was defined by dividing the concentration of boron in effluents (C_1) with influents (C_0) ($0.05 = C_1/C_0$).

The adsorption of boron in column using the prepared grafted adsorbent was first tested with flow rate of SV 15. This follows by flow rate of SV 50, SV 100, SV 200, and SV 400. For every flow rate, a new adsorbent packed into the column was prepared. Granular resin (Diaion) was also packed into the column and tested for SV 15, SV 50, and SV 100. The adsorbed boron in the column was eluted with 1 M hydrochloric acid at the same flow rate applied for the selected column-mode adsorption.

2.4. Determination of boron

The concentration of boron was measured using induced coupled plasma—optical emission spectroscopy (ICP-OES, Perkin Elmer—Optima 4300 DV). Boron standard solution of 1,000 mg/l was diluted to prepare three standard solutions containing 4, 8, and 15 mg/l. The calibration curve obtained was a linear with correlation coefficient of above 0.999. The concentration of boron in solution to be measured by the ICP was below 15 mg/l. The solution was diluted using ultra pure water (Milli-Q, Nippon Millipore Co, Japan) to below 15 mg/l if the concentration of boron in solution/sample was above the calibration range.

2.5. Scanning electron microscope analysis

The non-woven PE sample, GMA-grafted sample, and glucamine-modified adsorbent were observed with a scanning electron microscope (SEM, Hitachi SEMDX Type N) after coated with gold.

3. Result and discussion

3.1. Effect of radiation-induced grafting parameters

Fig. 1 shows that the degree of grafting was influenced by adsorbed dose, reaction time, and concentration of monomer. Highest degree of grafting, 310%, was obtained with the grafting conditions as follows: concentration of GMA, 10%; adsorbed dose, 100 kGy; and reaction time, 4 h. While lowest yield of grafting was obtained with the grafting conditions as follows: concentration of GMA, 5%; adsorbed dose, 30 kGy; and reaction time, 1 h. Hence, it could be concluded that, higher yield of radiation grafting could be obtained when the adsorbed dose, concentration of monomer used, and the reaction time applied were increased. Radiation allows radicals to be formed on the polymer and this will initiate grafting reaction. Therefore, high dose applied would give higher amount of radicals formed on the polymer. Subsequently, when high amount of monomer was used, this would result in higher degree grafting of the monomer onto the available reactive radicals.

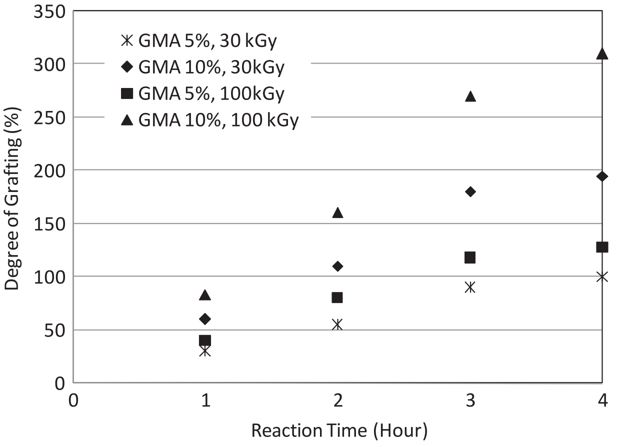

Fig. 1. Effect of the concentration of monomer, adsorbed dose and reaction time to the degree of grafting.

Grafting yield of about 200% was expected to give satisfactory requirement for the preparation of the metal adsorbent in the subsequent chemical modification step [9]. Although high dose irradiation could achieve high degree of grafting, it would also result in degradation of trunk polymer [10] and cross-linking [9]. In addition to that it will cause brittleness of the backbone polymer. It was also less economical to utilize high adsorbed dose. Therefore, the parameters selected for this study were as follows: concentration of GMA, 10%; absorbed dose, 30 kGy, and reaction time, 3 h. These grafting conditions gave 180% degree of grafting.

The grafted GMA onto the polymer backbone has reactive epoxy group. This reactive epoxy group of GMA was chemically modified via introduction of NMDG. The NMDG has a tertiary amine end and a polyol end. It could form very stable complex with boron [11,12].

3.2. Characterization of boron adsorbent: SEM analysis

Fig. 2 shows the image of PE non-woven polymer before grafting. (a) After grafted with GMA, the size of the all samples had increased from 13 to 25 μm. (b) The size increased of sample could be observed on all grafted samples. Further size increased of sample could also be observed after the grafted material was chemically modified by NMDG. (c) The density of NMDG was 2.2 mmol/g.

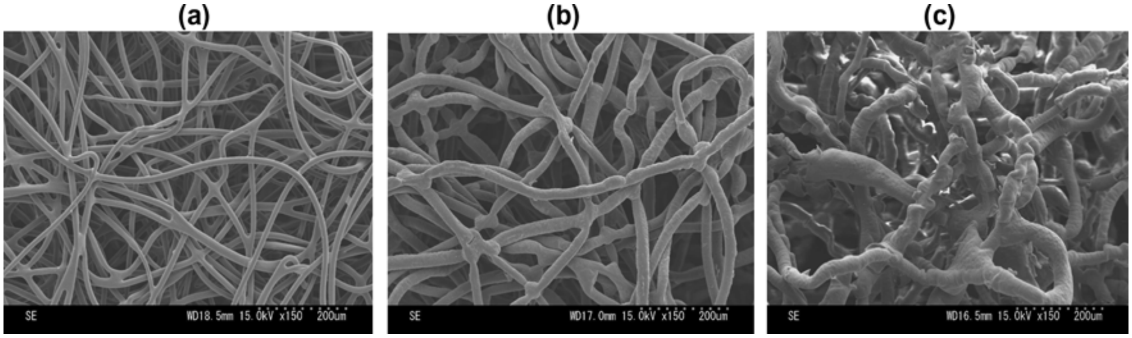

Fig. 2. SEM observation of (a) before grafting, (b) after grafting of GMA, and (c) NMDG adsorbent.

3.3. Batch-mode adsorption

The effect of pH on boron adsorption was examined from 2 to 11. As shown in Fig. 3, pH from 4 to 8 have highest adsorption capacity of boron. These values were slightly below 14.5 mg-B/g-adsorbent (the adsorption capacity of 14.5 mg-B/g-adsorbent was obtained after reaction time of 24 h at pH 6). The pH was the key factor in influencing the adsorption of boron. This was in agreement with other studies [13,14]. At concentration below 250 mg/l, boron exists mainly in the form of $B(OH)_3$ and $B(OH)_4^-$ [15]. Boron adsorption would lead to the production of proton ion (H^+) and this would result in restriction of boron adsorption at low pH. As the pH of the solution increased (close to neutral pH), concentration of boron in the form of $B(OH)_4^-$ would also increase and resulted in higher quantity of boron adsorbed. Further increase of pH to above 8 would produce more amount of OH^-. Subsequently, this would lead to decrease in boron adsorption due to the competition effect [16]. In addition to that, there was also an electrostatic repulsion between the $B(OH)_4^-$ ions and the negatively charged adsorbents where the complexation formed become weak.

3.4. Column-mode adsorption

The breakthrough curves were evaluated from SV 15 to SV 400, where pH and concentration of boron were fixed at 6.0 and 10.0 mg/l, respectively. Temperature (293 K) and dimension of column were kept constant. Fig. 4 shows the effect of SV to the breakthrough curve. It could be expected that, when higher flow rate was applied, the breakthrough curve obtained would be gradually shifted to the left side. Surprisingly, we did not observe this trend in this study.

The breakthrough curve did not display apparent changes in terms of the movement of the breakthrough curves to certain direction. To make the trend

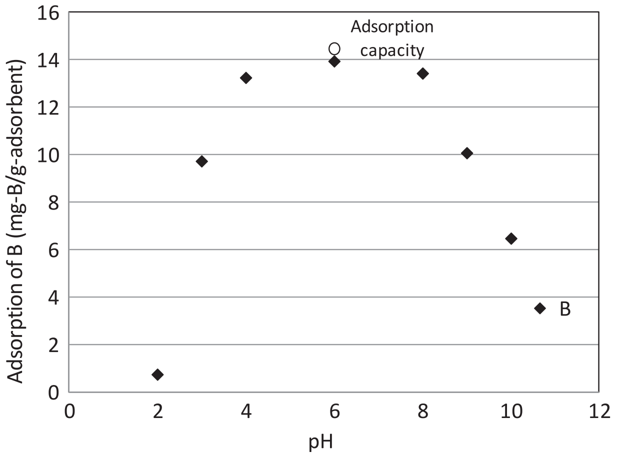

Fig. 3. Effect of the pH to amount of boron adsorbed (○ adsorption capacity where adsorbent immersed in boron solution for 24 h and ◆ adsorbent immersed in boron solution for 2 h).

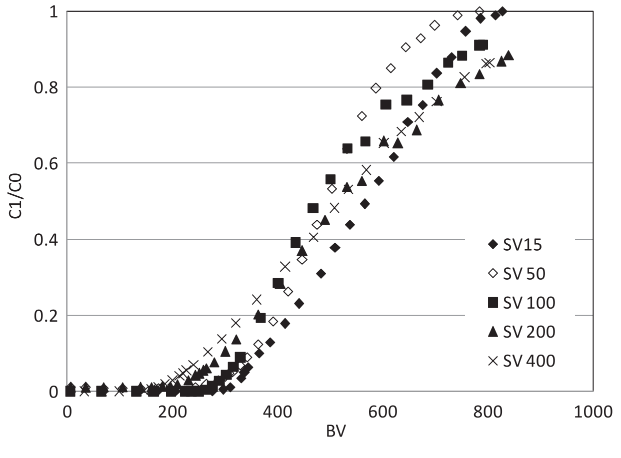

Fig. 4. Effect of the flow speed at SV 15, SV 50, SV 100, SV 200, and SV 400 to the breakthrough curve.

more visible, we have further assessing the breakthrough curve in Fig. 4 by calculating the total breakthrough point and total breakthrough capacity of each breakthrough curve (Fig. 5). As the SV increased from SV 15 to SV 400, total breakthrough capacity has reduced from 13.8 to 12.7 mg-B/g-adsorbent. This translated into 8% reduction of total breakthrough capacity and indicated that the increase of flow speed from SV 15 to SV 400 had marginal effect on the performance of the adsorbent.

No apparent trend of breakthrough curve could be observed when SV 15 was increased to SV 400 (Fig. 4). This was due to the marginal 8% reduction of total breakthrough capacity. This indicated that the prepared boron-selective adsorbent has high performance and capability to adsorb boron even at SV 400. The marginal 8% reduction of total breakthrough capacity perhaps was contributed from few factors. First, it was because of sufficient active sites on the adsorbent to adsorb boron even at very high flow speed.

Second, the fine non-woven PE polymer with diameter of about 13 μm could result in high diffusion rate of boron ions in the adsorbent. Subsequently, this contributes to high removal characteristic of grafted adsorbent compared to granular resin adsorbent. Fine diameter of about 13 μm as compared to granular resin with typical diameter of 0.5 mm would prevent the loss of applied pressure at high SV.

Third, the grafted adsorbents were evenly distributed in the column. Therefore, shifting or moving of the packed adsorbent inside the column was avoided. When high flow rate of up to SV 400 h^{-1} was applied, bypass of the flow of solution was prevented in the column.

Fourth, the even pores sizes at desirable diameter and large surface area (Fig. 2) also have contributed to the performance of the adsorbent. This type of structure arrangement was more effective compared to conventional granular resin in promoting efficient contact between boron (in the solution) and surface of the adsorbent. Subsequently, this has prevented the leakage of boron solution. In other words, this type of structure arrangement has promoted fast and efficient contact between boron solution and adsorbent. From Fig. 2(c), the adsorbent pores size was estimated to be 250 μm and below. The pore sizes of packed adsorbent in the column were expected to be less than 250 μm, due to pressure applied when adsorbents were packed into the column. Therefore, the size of the fine PE polymer used to prepare the adsorbent was appropriate. The interaction between adsorbent and boron solution was sufficient and efficient at SV 400, where total adsorption capacity only reduced 8%.

However, total breakthrough point capacity has reduced substantially from 8.3 to 5.5 mg-B/g-adsorbent (Fig. 5). This translated into 34% reduction of total breakthrough point capacity. Although the total breakthrough point capacity has reduced at higher percentage (34%), it only occurred at 218 BV. The breakthrough point capacity for SV 15 occurred at 330 BV (Fig. 6). The breakthrough point capacity of granular resin for SV 15 and SV 100 was 140 and 35 BV, respectively (Fig. 6). This is also in agreement to other works on granular resin [11,17]. This indicates that the prepared grafted adsorbent was performed at reasonable good level.

The higher percentage (34%) reduction of the total breakthrough point capacity perhaps was due to shortening of contact time between boron solution

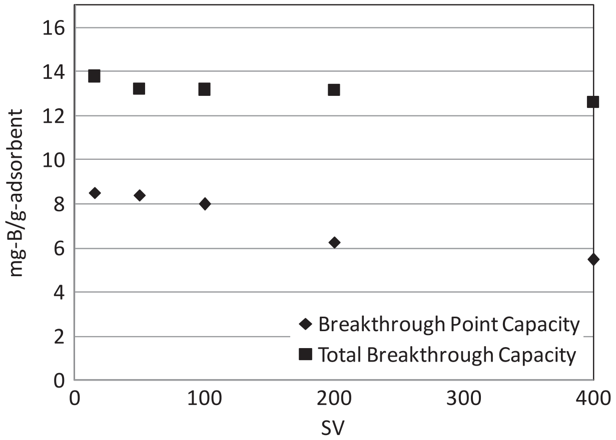

Fig. 5. Breakthrough point and breakthrough capacity at various SV.

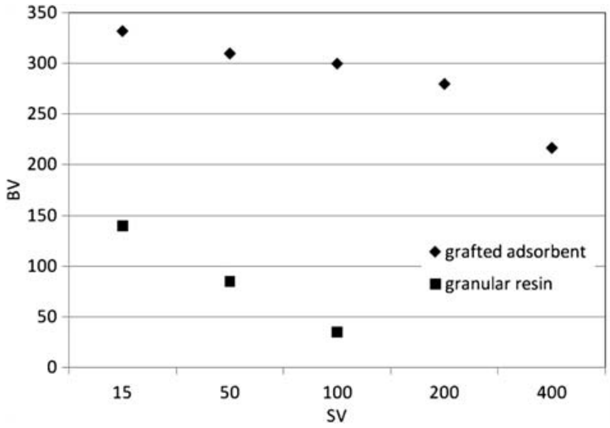

Fig. 6. BV at breakthrough point of various SV: comparison between grafted adsorbent and granular resin.

and adsorbent. Time for adsorption has reduced at high flow rate. Although the surface areas of adsorbent remain same, higher flow rate has prevented interaction/contact between boron solution and surface/area of adsorbent. This suggests that the boron solution might pass through existing passages that were already filled by earlier boron passed through it (without any surface interaction).

The prepared grafted adsorbent was capable to remove boron at very high flow rate. It could be potentially applied for removing boron found at low concentration in large amount of water. Processing time required for treatment could be reduced significantly.

3.5. Elution test

Fig. 7 shows the elution profile of boron eluted by 1 M HCl at SV 15 to SV 400. All adsorbed boron was eluted at 10 BV. It could be observed that desorption of boron from the adsorbent could be done irrespective of the flow rate. After desorbing the adsorbed boron, the adsorbent could be reused again. Although we have not evaluated the number of reusability of the same absorbent, the result of the adsorption and desorption presented in this study indicated that it could be reused for many times. The characteristics of wastewater, such as pH, level of suspended solid found in real wastewater and others, might influence the number of reusability. High number of reusability of the adsorbent could reduce the cost of treatment.

4. Conclusion

A new boron-selective adsorbent was synthesized using radiation graft polymerization technique. The prepared adsorption exhibits high adsorption and desorption performances. The total adsorption capacity (breakthrough curve) has only reduced 8% as the SV increased from SV15 to SV 400. Influence of the flow speed to the boron desorption is negligible. This shows that the prepared adsorbent was suitable to be applied in high speed/pressure operating environment of up to SV 400, while maintain the effectiveness and efficiency of the boron adsorption and desorption process. This would remarkably lead to the improvement of the treatment time, volume of feeding water, and eventually the cost of treatment.

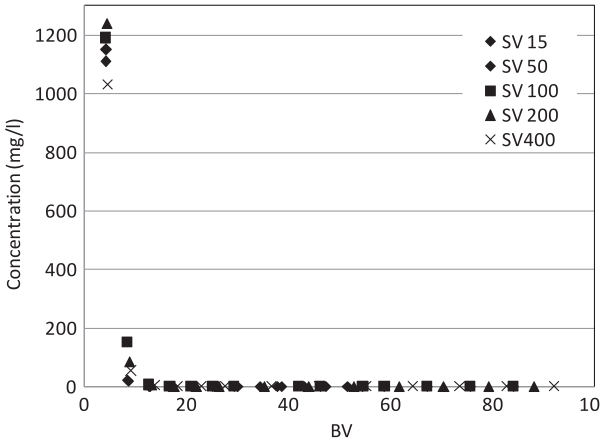

Fig. 7. Elution for SV 15, SV 50, SV 100, SV 200, and SV 400.

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References

[1] WHO, Guidelines for Drinking-Water Quality, fourth ed., Gutenberg, Malta, 2011.

[2] M.O. Simonnot, C. Castel, M. Nikolai, C. Rosin, M. Sardin, H. Jaufferet, Boron removal from drinking water with a boron selective resin: Is the treatment really selective? Water Res. 34 (2000) 109–116.

[3] M. Badruk, N. Kabay, H. Mordogan, U. Ipekoglu, Removal of boron from wastewater of geothermal power plant by selective ion exchange resins II: Column sorption–elution studies, Separ. Sci. Technol. 34(15) (1999) 2981–2995.

[4] N. Kabay, I. Yilmaz, S. Yamac, M. Yuksel, U. Yuksel, N. Yildirim, O. Aydogdu, T. Iwanaga, K. Hirowatari, Removal and recovery of boron from geothermal wastewater by selective ion exchange resins II: Field studies, Desalination 167 (2004) 427–438.

[5] N. Nadav, Boron removal from seawater reverse osmosis permeate utilizing selective ion exchange resins, Desalination 124 (1999) 131–135.

[6] N. Kabay, S. Sarp, M. Yuksel, M. Kitis, H. Koseoglu, O. Arar, M. Bryjak, R. Semiat, Removal of boron from SWRO permeate by boron selective ion exchange resins containing n-methyl glucamine groups, Desalination 223 (2006) 49–56.

[7] C.Y. Yan, W.T. Yi, P.H. Ma, X.C. Deng, F.Q. Li, Removal of boron from refined brine by using selective ion exchange resins, J. Hazard. Mater. 154 (2008) 564–571.

[8] A.M. Wachinski, J.E. Etzel, Environmental Ion Exchange, Lewis, New York, NY, 1996.

[9] N. Seko, L.T. Bang, M. Tamada, Syntheses of amine-type adsorbents with emulsion graft polymerization of glycidyl methacrylate, Nucl. Instrum. Methods Phys. Res., Sect. B 265 (2007) 146–149.

[10] A. Alberti, S. Bertini, G. Gastaldi, N. Iannaccone, D. Macciantelli, G. Torri, E. Vismara, Electron beam irradiated textile cellulose fibers: ESR studies and derivatisation with glycudyl methacrylate (GMA), Eur. Polym. J. 41 (2005) 1787–1797.

[11] N. Kabay, I. Yılmaz, S. Yamac, S. Samatya, M. Yuksel, U. Yuksel, M. Arda, M. Sağlam, T. Iwanaga, K. Hirowatari, Removal and recovery of boron from geothermal wastewater by selective ion exchange resins I: Laboratory tests, React. Funct. Polym. 60 (2004) 163–170.

[12] H.F. Ayyildiz, H. Kara, Boron removal by ion exchange membranes, Desalination 180 (2005) 99–108.

[13] Y. Inukai, Y. Tanaka, T. Matsuda, N. Mihara, K. Yamada, N. Nambu, O. Itoh, T. Doi, Y. Kaida, S. Yasuda, Removal of boron (III) by N-methylglucamine-type cellulose derivatives with higher adsorption rate, Anal. Chim. Acta 511 (2004) 261–265.

[14] N. Ozturk, T.E. Kose, Boron removal from aqueous solutions by ion exchange resin: Batch studies, Desalination 227 (2008) 233–240.

[15] P.P. Power, G.W. Woods, The chemistry of boron and its speciation in plants, Plant Soil 193 (1997) 1–13.

[16] E.P.A, Health and Environmental Effects Document for Boron and Boron Compounds, U.S. Environmental Protection Agency, Washington, DC, EPA 6008-91015, 1991.

[17] K.W. Baek, S.H. Song, S.H. Kang, Y.W. Rhee, C.S. Lee, B.J. Lee, S. Hudson, T.S. Hwang, Adsorption kinetics of boron by anion exchange resin in packed column bed, J. Ind. Eng. Chem. 13 (2007) 452–456.