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# Effect of synthesis conditions of polyallylamine-beads-glucose (PAA-Glu) on boron adsorption

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**Abstract** In this study, we assessed the boron adsorption characteristic of our synthesized adsorbent: polyallylamine-beads-glucose (PAA-Glu) by using the adsorption amount and adsorption site availability (ASA), and determined the optimum conditions for PAA-Glu synthesis. ASA is our proposed indicator and it expresses the percentage of the experimental equilibrium adsorption in relation to the theoretical equilibrium adsorption and indicates the availability of adsorption sites (hydroxyl groups) on adsorbents. We investigated the effects of the degree of cross-linking (20, 40 and 60 %), the introduction amount of $\alpha$-D-glucose (40, 60 and 80 %), and the introduction temperature (30–150 °C) as regards PAA-Glu on the boron adsorption amount. The boron adsorption amount for PAA-Glu (20 % cross-linked, 30 °C) was superior to that for another degree of cross-linked PAA-Glu. However, the ASA for PAA-Glu (60 % cross-linked, 30 °C) exhibited the best value in this synthesized PAA-Glu. Furthermore, we examined the introduction temperature at which glucose was introduced to PAA-Glu (20 % cross-linked) in the 30–150 °C range, and we confirmed that the optimum temperature range for the synthesis of PAA-Glu was 60–80 °C. We found that controlling the space between the main chains of the polymer by using a spacer such as a cross-linker allowed boron molecules to come and go and led to an improvement in the boron adsorption amount and ASA.

**Keywords** Boron · Removal · Adsorption · Polyallylamine (PAA) · Saccharide

**Abbreviations**

| | |
|---|---|
| PVA | polyvinyl alcohol |
| EGDE | ethylene glycol diglycidyl ether |
| PAA | polyallylamine |
| PAA beads | polyallylamine beads |
| PAA-Glu | polyallylamine-beads-glucose |
| ICP-AES | inductively coupled plasma atomic emission spectroscopy |
| ASA | adsorption site availability |

## 1 Introduction

Boron occurs naturally in seawater and hot spring water and is commonly present as an element. Boron or boron compounds have a wide variety of applications ranging from medicines to industrial products. Recently, boron concentration in wastewater has increased with the increasing use of boron compounds, and concern has grown regarding boron's detrimental effect on the human body (Parks and Edwards 2005; Nable et al. 1997).

There are various techniques for removing boron from aqueous solutions (Xu and Jiang 2008; Yilmaz et al. 2005, 2007; Cengeloglu et al. 2008; Qin et al. 2005; Turek et al. 2007; Matsumoto et al. 1997; Spicer and Strickland 1958;

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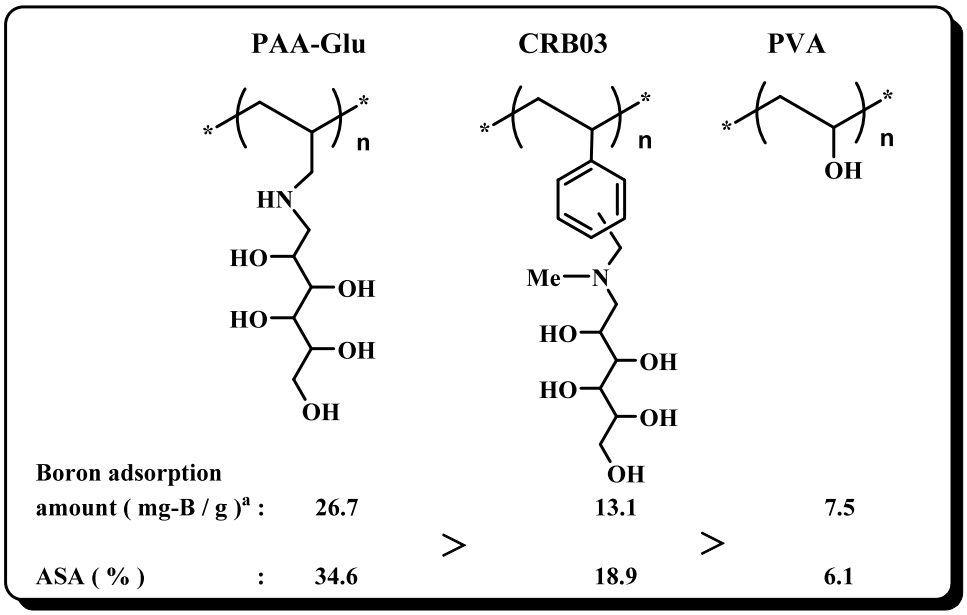


**Fig. 1** Structure and results of assessment for each adsorbent

[a]: All of the adsorption measurements were carried out in boron solution (250ppm) and the optimum pH range (PAA-Glu: pH9, CRB03 and CRB05: pH5 and PVA: pH13) (Harada et al. 2011).

Kose and Oztuek 2008; Yoshimura et al. 1998; Seki et al. 2006; Ozturk and Kavak 2008; Kaftan et al. 2005; Celik et al. 2008; Sabarudin et al. 2005), and we focused on a removal method that uses adsorbents. Many adsorbents for the selective removal of boron contain a large number hydroxyl groups in their molecules to make it possible to utilize the strong affinity between boron and hydroxyl groups (Garcia-Soto and Camacho 2005; Labouriau et al. 2006).

We have already reported adsorption site availability (ASA) as an indicator for assessing boron adsorbents, based on an investigation of the relationship between boron adsorption amount and adsorption sites (hydroxyl groups) that we undertook by studying the boron adsorption characteristic as regards polyvinyl alcohol (PVA) (Harada et al. 2011). We compared the adsorption characteristic of PVA with those of commercially available adsorbents (CRB03, CRB05) and our synthesized adsorbent (polyallylamine-beads-glucose (PAA-Glu)) by assessing the boron adsorption amount and the ASA. CRB03, CRB05 and PAA-Glu with sugar moiety exhibited a clearly higher boron adsorption capacity and ASA value than PVA (as shown in Fig. 1).

Sugars have been commonly used for the removal of boron (Parks and Edwards 2005; Xu and Jiang 2008; Yoshimura et al. 1998; Kaftan et al. 2005; Sabarudin et al. 2005). Many commercially available adsorbents, such as CRB03, CRB05 and IRA743 (Rohm and Haas Co.) (Garcia-Soto and Camacho 2005), have *N*-methylglucamine groups in their molecules. So, when developing adsorbents using polyallylamine (PAA), we introduced sugar moieties into the amino groups on PAA, because the hydroxyl groups were located at a point far from the main chain of the compound. Although PAA beads modified with sugars have already been reported (Kaida et al. 2002, 2003), there has been no detailed study of the reaction conditions for the formation of PAA beads modified with sugars. We found that it was effective for boron adsorbents to have many hydroxyl groups such as sugars and to maintain an appropriate distance between polymer chains. Therefore, the PAA-Glu synthesis conditions required further investigation by performing an assessment based on the boron adsorption characteristic.

In this study, we investigated the effect of the PAA-Glu synthesis conditions in relation to boron adsorption. We optimized the amount of added reagents (cross-linker and $\alpha$-D-glucose) and the reaction temperature. First, the effects of the degree of cross-linking were investigated on the conjugated amount of $\alpha$-D-glucose. Next, by using reductive alkylation, we optimized the introduction temperature of $\alpha$-D-glucose for 20 % cross-linked PAA beads. Finally, the adsorption capacity and ASA of PAA-Glu were compared with those of other commercial adsorbents.

The adsorption capacity and the ASA were improved by optimizing the synthesis conditions for PAA-Glu. We found that we were able to develop a boron adsorbent with a high boron adsorption capacity and a high ASA value by selecting the optimum conformation for the adsorbents.

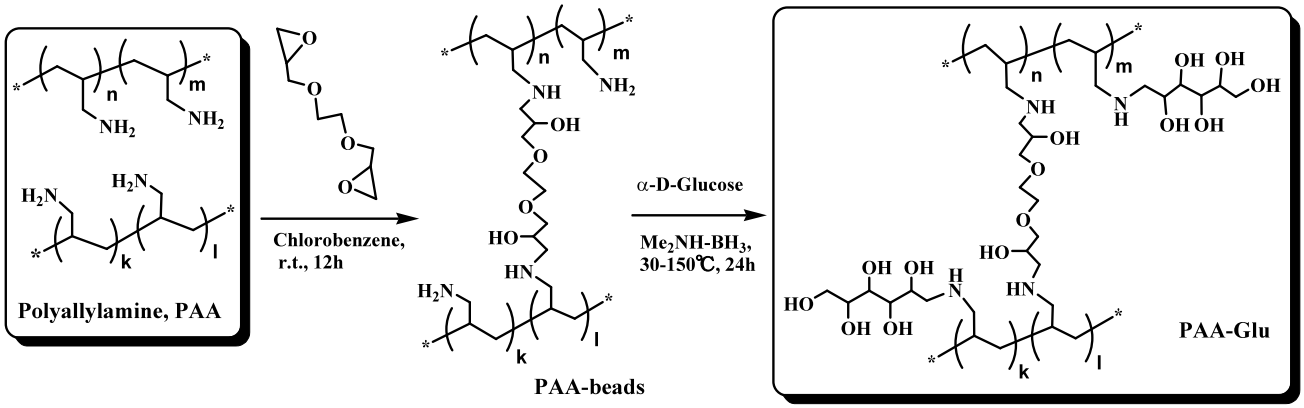


**Fig. 2** Cross-linkage of PAA and introduction of $\alpha$-D-glucose

## 2 Experiments

### 2.1 Chemicals

Polyallylamine hydrochloride (PAA) ($M_w$ = 150,000) (40.4 %w/v solution) was obtained from Nitto Boseki Co. Boron standard solution (1000 mg/l B) was purchased from Merck Co., Ltd. Chlorobenzene (99.5 %), dimethylamine borane (DMAB) (95 %) and polyvinyl alcohol (PVA) 2,000 were purchased from Kishida Chemical Co., Ltd. Ethylene glycol diglycidyl ether (EGDE) was purchased from Tokyo Chemical Industry Co., Ltd. $\alpha$-D-glucose was purchased from Sigma-Aldrich. *N*-Methylglucamine-type resins (DIAION: CRB03, CRB05) were supplied by Mitsubishi Chemical Corporation. Milli-Q water (Nihon Millipore K. K.) was used to prepare all the solutions.

### 2.2 Synthesis of polyallylamine-beads-glucose (PAA-Glu)

PAA and $\alpha$-D-glucose as starting materials are both soluble in water, so we needed to perform an insoluble treatment at some stage. PAA was insolubilized with a cross-linking agent, and then the insolubilized PAA was modified with sugars.

We used EGDE, which has an epoxy group at both ends, as a cross-linking agent. PAA beads were synthesized by connecting amino groups to each other using EGDE. A cross-linker with an epoxy group in its molecule is highly responsive to amino groups. When introducing $\alpha$-D-glucose, we selected reductive alkylation by DMAB, and then a stable C-N single bond was formed from unstable imine bond (Mitts and Hixon 1944; Thorpe and Baynes 2003). A diagram of the PAA-Glu synthesis technique is shown in Fig. 2.

#### *2.2.1 Synthesis of PAA beads*

40.4 %w/v aqueous polyallylamine hydrochloride 75.02 g (-$NH_2$, 0.530 mol) was mixed with 1 mol/L NaOH (256 mL) in a 1L round-bottomed flask and stirred for 20 minutes at room temperature. EGDE (7.76 mL, 0.0530 mol) was added to the solution and stirred vigorously for 2.5 minutes. The reaction solution was immediately poured into chlorobenzene (500 mL), before it turned completely into a gel, and then stirred continuously for 12 hours at room temperature (Zeng and Ruckenstein 1998; Ngah et al. 2002). The solution was filtered and evaporated to remove as much chlorobenzene as possible. 20 % cross-linked PAA beads were obtained as a translucent gel. The PAA beads after complete drying were used for the subsequent reaction.

#### *2.2.2 Synthesis of PAA-Glu*

Synthesized PAA-Glu is expressed as follows:

PAA-Glu-*X*-*Y*

*X*: the degree of cross-linking (%), *Y*: the introduction temperature of $\alpha$-D-glucose ($^{o}$C).

PAA-Glu was prepared according to the following procedure reported by Kaida et al. (2002, 2003). 20 % cross-linked PAA beads were dispersed in 200 mL of water. $\alpha$-D-Glucose (76.45 g, 0.424 mol) was dissolved completely in 400 mL of water, and this solution was then added to 20 % cross-linked PAA-beads suspended in solution and stirred. Then, DMAB (25.00 g, 0.424 mol) was added to the suspension and stirred continuously for 24 hours at 30–150 °C. The reaction at 130 and 150 °C was carried out by using an autoclave reactor. The reaction suspension was filtered and repeatedly washed with 1 mol/L HCl and Milli-Q water. Next, these residual gel-beads were completely neutralized with 1 mol/L NaOH, and then repeatedly washed with Milli-Q water. Finally, the gel-beads were washed with MeOH and dried under reduced pressure at room temperature. A white solid consisting of PAA-Glu-20–30 (72.1 g) was obtained. A diagram of the PAA-Glu synthesis mechanism is shown in Fig. 2. The amounts of reagents required to synthesize PAA beads and PAA-Glu are shown in Table 1.

**Table 1** The amount of reagents required to synthesize PAA beads and PAA-Glu

| | PAA (g/mol) | 1M NaOHaq (mL) | EGDE (mL/mol) | Chloro-benzene (mL) | α-D-Glucose (g/mol) | DMAB (g/mol) |
|---|---|---|---|---|---|---|
| PAA-Glu-20-30 | 75.02/0.530 | 256 | 7.76/0.0530 | 500 | 76.45/0.424 | 25.00/0.424 |
| PAA-Glu-40-30 | 50.30/0.356 | 178 | 10.41/0.0711 | 500 | 38.44/0.213 | 12.57/0.213 |
| PAA-Glu-60-30 | 71.80/0.508 | 406 | 22.29/0.152 | 900 | 36.58/0.203 | 11.96/0.203 |

## 2.3 Characterization of PAA beads and PAA-Glu

To estimate the degree of cross-linking for PAA beads, the introduction yield of α-D-glucose and the number of hydroxyl groups, the chemical compositions of PAA, PAA beads and PAA-Glu were confirmed with a CE Instruments EA1110 elemental analyzer. The estimation procedure was as follows:

### *2.3.1 Degree of cross-linking for PAA beads*

The carbon and nitrogen content of the PAA and PAA beads was obtained from an elemental analysis. In the PAA beads, the amount of nitrogen atoms in PAA is not changed by the cross-linking. So, as a reference to the nitrogen content, the difference between the carbon content of the PAA and PAA beads was calculated from the analysis data. We assumed that the increased amount was equivalent to the amount of reacted cross-linker. We express the actual carbon and nitrogen content of the PAA and PAA beads as follows: $C_{PAA}$, $N_{PAA}$, $C_{beads}$ and $N_{beads}$. Furthermore, we express the theoretical carbon and nitrogen content of the PAA and PAA beads as follows: $C_{PAA(t)}$, $N_{PAA(t)}$, $C_{beads(t)}$ and $N_{beads(t)}$. The degree of cross-linking for PAA beads was calculated using the following formula:

$$\begin{aligned}&\text{The actual degree of cross-linking for PAA beads (\%)}\\&= \mathrm{TDC}(\%) \times \left[C_{beads} - (N_{beads} \times C_{PAA}/N_{PAA})\right]\\&\quad /\left[C_{beads(t)} - (N_{beads(t)} \times C_{PAA(t)}/N_{PAA(t)})\right] \qquad (1)\end{aligned}$$

TDC(%): the theoretical degree of cross-linking (in this study: 20, 40 or 60 %).

### *2.3.2 α-D-Glucose content for PAA-Glu*

The α-D-glucose content was also estimated from the composition formula and the chemical compositions. The content was calculated from the difference between the carbon content of the PAA beads and that of the PAA-Glu, which was based on elemental analysis data. In addition to Sect. 2.3.1, we express the carbon and nitrogen content of the PAA-Glu (actual and theoretical) as follows: $C_{Glu}$, $N_{Glu}$, $C_{Glu(t)}$ and $N_{Glu(t)}$. The introduced amount of α-D-glucose for PAA-Glu was calculated using the following formula:

$$\begin{aligned}&\text{The introduced amount of α-D-glucose for PAA-Glu (\%)}\\&= \mathrm{TAG}(\%) \times \left[C_{Glu} - (N_{Glu} \times C_{beads}/N_{beads})\right]\\&\quad /\left[C_{Glu(t)} - (N_{Glu(t)} \times C_{beads(t)}/N_{beads(t)})\right] \times 100 \qquad (2)\end{aligned}$$

TAG(%): the theoretical amount of added α-D-glucose (in this study: 40, 60 or 80 %).

### *2.3.3 Number of hydroxyl groups for each adsorbent*

The procedure for estimating the number of hydroxyl groups was described in our previous paper (Harada et al. 2011). The number of hydroxyl groups was calculated using the following formula:

$$\begin{aligned}&\text{The number of hydroxyl groups (unit/g)}\\&= \left\{\left[C_{Glu} - (N_{Glu} \times C_{beads}/N_{beads})\right] \times 5 \times N_A\right\}\\&\quad /(100 \times 12.011 \times 6) \qquad (3)\end{aligned}$$

5: the number of hydroxyl groups in one glucose group, $N_A$: Avogadro number, 100: percentage figure, 12.0011: atomic weight of carbon and 6: the number of carbon containing glucose groups.

## 2.4 Adsorption experiment

Solutions containing 250 ppm boron were prepared from boron standard solution (1000 ppm) at pH 2–13, and then these solutions were used as simulated boron wastewater. Given amounts of adsorbents (0.0500–1.500 g) were added to the boron solutions (50 mL) and stirred at 120 rpm and 25 °C. Batch adsorption experiments lasting 24 hours were carried out for all adsorbents. The adsorption was performed long enough after equilibrium had been reached, since the adsorption experiment was designed to obtain the adsorption isotherm of boron. The solutions were filtered and the concentration of the boron remaining in the solutions was measured by inductively coupled plasma atomic emission spectroscopy (ICP-AES, SII NanoTechnology Inc., SPS7800).

**Table 2** The adsorption amounts and ASA for PAA-Glu and other adsorbents

| Adsorbent | Actual degree of cross-linking (%) | Introduction amount of α-D-glucose (%) | Number of hydroxyl groups (unit/g) | Experimental equilibrium adsorbed amount (mg B/g-adsorbent) | Theoretical equilibrium adsorbed amount (mg B/g-adsorbent) | ASA (%) |
|---|---|---|---|---|---|---|
| PAA-Glu-20-30 | 18.49 | 58.67 | $8.59 \times 10^{21}$ | 77.13 | 26.50 | 34.36 |
| PAA-Glu-20-40 | 17.90 | 65.38 | $9.57 \times 10^{21}$ | 85.93 | 26.04 | 33.30 |
| PAA-Glu-20-50 | 16.57 | 65.67 | $9.61 \times 10^{21}$ | 86.29 | 27.28 | 31.61 |
| PAA-Glu-20-60 | 18.06 | 60.25 | $8.85 \times 10^{21}$ | 79.47 | 30.16 | 37.95 |
| PAA-Glu-20-70 | 20.74 | 69.55 | $10.18 \times 10^{21}$ | 91.41 | 32.92 | 36.03 |
| PAA-Glu-20-80 | 20.74 | 69.98 | $10.24 \times 10^{21}$ | 91.95 | 32.74 | 35.61 |
| PAA-Glu-20-90 | 17.54 | 72.12 | $10.55 \times 10^{21}$ | 94.73 | 32.34 | 34.14 |
| PAA-Glu-20-100 | 17.54 | 74.10 | $10.84 \times 10^{21}$ | 97.33 | 32.67 | 33.57 |
| PAA-Glu-20-130 | 18.89 | 92.80 | $13.58 \times 10^{21}$ | 121.94 | 5.27 | 4.32 |
| PAA-Glu-20-150 | 18.89 | 96.11 | $14.06 \times 10^{21}$ | 126.25 | 4.29 | 3.40 |
| PAA-Glu-40-30 | 26.93 | 51.18 | $8.09 \times 10^{21}$ | 72.64 | 20.33 | 27.99 |
| PAA-Glu-60-30 | 53.08 | 23.32 | $4.01 \times 10^{21}$ | 36.01 | 16.90 | 46.93 |
| CRB03 | – | – | $7.72 \times 10^{21}$ | 69.32 | 14.65 | 21.13 |
| CRB05 | – | – | $7.85 \times 10^{21}$ | 70.49 | 16.14 | 22.90 |
| PVA ($n = 2000$) | – | – | $13.68 \times 10^{21}$ | 122.84 | 7.51 | 6.11 |

## 3 Results and discussion

### 3.1 Characterization of PAA, PAA beads and PAA-Glu

#### *3.1.1 Reaction yields of EGDE and α-D-glucose*

The degree of cross-linking and the α-D-glucose content were derived from the carbon and nitrogen content for PAA, PAA beads and PAA-Glu as described in Sects. 2.3.1 and 2.3.2. The results are shown in Table 2.

The degree of cross-linking was selected as 20, 40 and 60 %. As regards the content of α-D-glucose, 75–80 % of the total amount of added α-D-glucose was conjugated to 20 and 40 % cross-linked PAA beads. On the other hands, only 60 % of the added α-D-glucose was conjugated to 60 % cross-linked PAA beads with a high degree of cross-linking. Because amino groups on PAA were consumed by the connection with EGDE, the loss of free amino groups led to a decrease in the frequency with which collisions occurred between amino groups and α-D-glucose. So the amount of α-D-glucose introduced into the 60 % cross-linked PAA beads decreased.

We used 20 % cross-linked PAA beads to investigate the effect of the introduction temperature on the boron adsorption amount. The actual degree of cross-linking for PAA-Glu-20-*Y* ($Y = 30$–$150$) is shown in Table 2. In our investigation of the glucose introduction temperature, the introduced amount once decreased at 60 °C, and then increased with increasing temperature. However, the introduced amount was calculated as more than the amount of added glucose at 130 and 150 °C. The glucose content were higher than the added amount because amino groups derived from PAA were eliminated from its structure by the high temperature and pressure conditions, or some by-products, such as polymerization products, were produced under this condition.

The elemental analysis for this characterization is very sensitive and can be affected by remaining organic solvents and the other contaminants included in a sample. Particularly close attention was paid to washing and drying the adsorbents in this work. In this measurement, PAA beads and PAA-Glu formed the compound with which the cross-linking agent and α-D-glucose reacted, with PAA as a starting material. The nitrogen content derived from PAA was constant before and after each reaction, so there was an increase in the carbon content derived from the cross-linking agent and α-D-glucose. Therefore, we noted changes in the contained amounts of carbon and nitrogen to investigate the progress in each reaction. PAA beads and PAA-Glu had many hydrophilic groups in their molecules and a hygroscopic nature. However, even if the adsorbents contained a small amount of water, their carbon and nitrogen content was unaffected. The error for measurements of the same sample in the elemental analysis result was within 3 %.

#### *3.1.2 Estimation of number of hydroxyl groups for other adsorbents*

The number of hydroxyl groups containing each adsorbent was estimated. In the estimation procedure, we used the

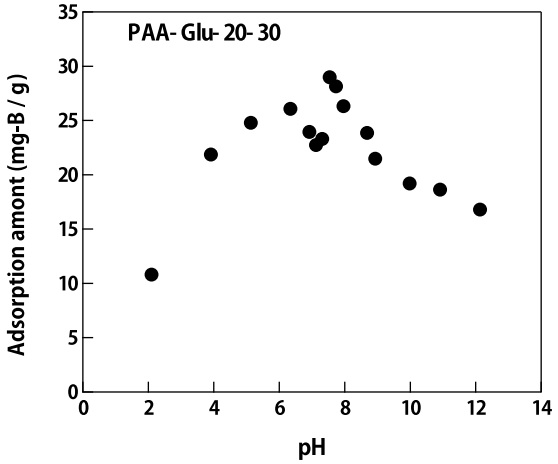


**Fig. 3** Boron adsorption amount for PAA-Glu-20-30 (100 mg) in boron simulated wastewater with different pH values

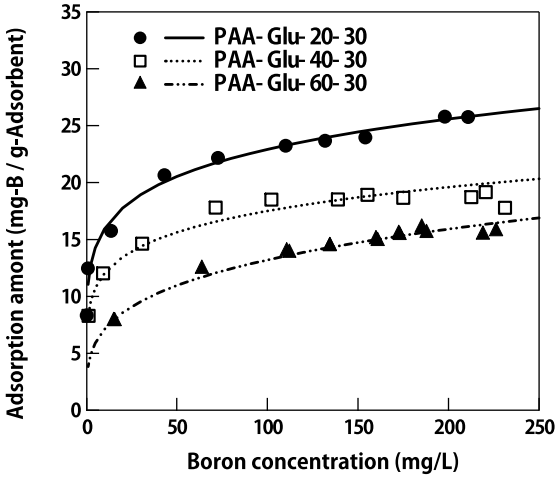


**Fig. 4** Boron adsorption isotherms and fitted Freundlich isotherms for PAA-Glu-$X$-30 ($X = 20$, 40, 60) (boron solution (250 ppm, pH 7.5)) (*symbols* indicate adsorption isotherms from experiments, *lines* indicate analysis results from the Freundlich equation)

composition formula described in Sect. 2.3.3 and the elemental analysis results. The number of hydroxyl groups for each adsorbent is shown in Table 2. When the introduction temperature was higher than 70 °C, the number of hydroxyl groups on PAA-Glu exceeded $10 \times 10^{21}$ unit/g.

## 3.2 Boron adsorption on PAA-Glu

In general, the boron adsorption properties, such as adsorption capacity, the shape of adsorption isotherms, and the adsorption rate, could depend on the boron concentration, especially at very high concentrations. We measured the boron adsorption isotherms over a wide concentration range and confirmed that there was no difference in the boron adsorption behavior at concentrations lower than 250 ppm. Consequently, our boron adsorption measurements were performed at concentrations below 250 ppm. This is slightly higher than 230 ppm, which is the concentration limit for effluent discharged into Japanese sea water.

### *3.2.1 Optimum pH for PAA-Glu in boron adsorption*

To check the optimum pH range for PAA-Glu, the boron adsorption amount was compared for a constant amount of adsorbent, namely, PAA-Glu-20-30, and using the boron simulated wastewater with a different of pH values. The influence of pH on boron adsorption is shown in Fig. 3.

The optimum pH range was around 7.5 for PAA-Glu-20-30. All of the adsorption measurements described below were carried out at the optimum pH 7.5 for each PAA-Glu.

### *3.2.2 Comparison of degree of cross-linking with EGDE*

In this study, we undertook the insoluble treatment of PAA by using cross-linking (EGDE). PAA beads were formed when EGDE equivalent to 20, 40 and 60 % with respect to the total number of amino groups was added to the PAA solution. PAA beads with different degrees of cross-linking were modified with $\alpha$-D-glucose equivalent to 40, 60 and 80 % with respect to the total number of amino groups. Using the obtained PAA-Glu-$X$-30 ($X = 20$, 40, 60), we performed boron adsorption experiments and investigated the effects of the degree of cross-linking by EGDE. Corresponding boron adsorption isotherms are shown in Fig. 4.

Then, we analyzed the adsorption isotherms using the Freundlich equation,

$$q = k_f C^{1/n} \tag{4}$$

where $q$ is the adsorption amount (mg/g), $k_f$ is the adsorption constant (L/g), $C$ is the boron concentration (mg/L) and $1/n$ is an arbitrary parameter (Mathialagan and Viraraghavan 2002; Ho et al. 2005).

The Freundlich equation provided a better fit for PAA-Glu as described in our previous paper (Harada et al. 2011). PAA-Glu-20-30 with the smallest degree of cross-linking exhibited larger adsorption constants than other degrees of PAA-Glu cross-linking. That is, the boron adsorption constants became larger as the degree of cross-linking became smaller.

Here, to assess the performance of adsorbents, in addition to investigating the equilibrium adsorbed amount, we introduce an indicator for assessing the boron adsorption objectively. We have already reported adsorption site availability (ASA), which is defined as follows;

$$\begin{aligned}\text{ASA}\ (\%) = &\ (\text{equilibrium adsorbed amount from} \\ &\ \text{adsorption experiment}) \\ &/(\text{theoretical equilibrium adsorbed amount}) \\ &\times 100 \end{aligned} \tag{5}$$

We calculated this ASA for the examined adsorbents. Employing the ASA, we could compare adsorption sites (hydroxyl groups) within adsorbents and the actual number of adsorption sites that utilized boron adsorption. In this comparison of ASA, we assumed that boron adsorption was only induced on the hydroxyl group as the adsorption site, and we ignored the effect of nitrogen atoms (amino group). Furthermore, many researchers involved in work on boron adsorption have adopted various combination patterns (Sahin 1996; Kabay et al. 2007; Okay et al. 1985; Qi et al. 2002; Sinton 1987; Geffen et al. 2006), and then these conformations depend on the boron concentration, pH and other factors. However, we assumed that boron adsorption was induced between one boron molecule (tetrahydroxyboric acid) and two hydroxyl groups. Further details of the ASA can be found in our previous paper (Harada et al. 2011). The ASA for PAA-Glu-$X$-30 ($X = 20$, 40, 60) is shown Table 2.

The adsorption capacity for PAA-Glu-20-30 was larger than for other types of PAA-Glu. The ASA for PAA-Glu-60-30 exhibited the largest value of 46.93 %, and this result showed that hydroxyl groups on PAA-Glu-60-30 were efficiently utilized for boron adsorption. This result suggests that it became possible for boron molecules to access the introduced glucose easily, because a certain distance was maintained between polymer chains by the high degree of cross-linking. That is, by using ASA, we confirmed that it is important to control the position at which glucose is introduced on PAA-Glu appropriately.

Here, in our assessment of adsorbents using adsorption amount and ASA, the former results were given priority over the latter. So, of these three types of PAA-Glu, we decided that PAA-Glu-20-30 exhibiting a large boron adsorption amount was a better adsorbent than PAA-Glu-60-30 with a high ASA value.

### 3.2.3 *Influence of introduction temperature on α-D-glucose*

The introduction temperature for 20 % cross-linked PAA beads was set at 40–150 °C, and then reductive alkylation was carried out at various temperature. Using the obtained PAA-Glu-20-$Y$ ($Y = 30$–150), we performed boron adsorption experiments and investigated the influence of the introduction temperature values. Boron adsorption isotherms for PAA-Glu-20-$Y$ ($Y = 30$–150) are shown in Fig. 5.

At introduction temperatures of 30–100 °C, each PAA-Glu exhibited a large boron adsorption capacity and provided a good fit for the Freundlich equation. However, at introduction temperatures of 130 and 150 °C, very little boron adsorption was induced and $k_f$ from the Freundlich equation exhibited a clearly smaller value than other types of PAA-Glu. The ASA for PAA-Glu-20-$Y$ ($Y = 30$–150) is

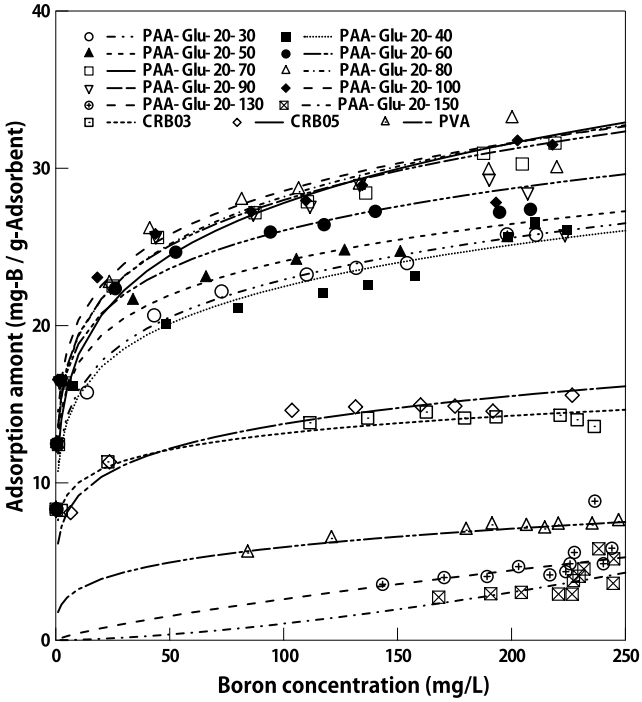


**Fig. 5** Boron adsorption isotherms for PAA-Glu-20-$Y$ ($Y = 30$–150) and other adsorbents (boron solution (250 ppm)) (*symbols* indicate adsorption isotherms from experiments, *lines* indicate analysis results from the Freundlich equation)

shown in Table 2. The boron adsorption amount exceeded 30 mg B/g in PAA-Glu synthesized at 60–100 °C. The ASA was more than 35 % in PAA-Glu synthesized at 60–80 °C.

The reductive alkylation was carried out in aqueous solution, so we used an autoclave unit at a temperature exceeding 100 °C. The reaction was carried out at high temperature and pressure. Therefore, we considered that the PAA-Glu structure collapsed, or the amino groups on the PAA were eliminated under this condition. In the calculation using the elemental analysis results, due to a change in the nitrogen content employed as the basis for the calculations, the carbon content ratio in a molecule was increased. Therefore, the calculated number of hydroxyl groups became large. Consequently, the number of actual adsorption sites fell to an extremely low level, and the boron adsorption amount was about 5 mg B/g. Generally, in a reaction between amino groups and a reducing sugar, the Maillard reaction is promoted by heating (Nurstern 1981; Boekel 1998; Mastrocola and Munari 2000). In this introduction reaction of α-D-glucose, as the synthesized PAA-Glu was pale yellow above 60 °C, we considered that the Maillard reaction proceeded in addition to reductive alkylation. Furthermore, the reductive alkylation and the Maillard reaction were promoted by heating at 60–100 °C, so the number of hydroxyl groups was greatly increased by the combined effects. Therefore, the adsorption amount and ASA exhibited considerable improvement.

From our investigation of the glucose introduction temperature, we confirmed that the optimum temperature range for $\alpha$-D-glucose introduction was 60–80 °C for PAA-Glu.

### 3.3 Comparative discussion of other adsorbents

From our investigation described above, we decided that PAA-Glu-20-$Y$ ($Y = 60$–$80$) were a superior adsorbent and we compared it with other adsorbents (CRB03, CRB05 and PVA). Boron adsorption isotherms for PAA-Glu-20-$Y$ ($Y = 60$–$80$), CRB03, CRB05 and PVA are shown in Fig. 5. The adsorption amount and the ASA for each adsorbent is shown in Table 2.

We performed adsorption experiments in the optimum pH range (5–7 for CRB03, CRB05 and 13 for PVA) (Harada et al. 2011).

PVA had the largest number of hydroxyl groups among these adsorbents (Wolf and Suter 1984), but it was insufficient for effective boron removal. Even, the commercially available adsorbents (CRB03 and CRB05) had a considerable number of unexploited adsorption sites. PAA-Glu exhibited a larger adsorption capacity and ASA than CRB03, CRB05 and PVA. PAA-Glu-20-$Y$ ($Y = 60$–$80$) also showed a considerable improvement compared with PAA-Glu that we reported in our previous paper (Harada et al. 2011).

In Kaida et al.'s paper describing a procedure for synthesizing PAA, they mentioned that the optimum temperature range for reductive alkylation is 35 °C. Their synthesized PAA-Glu (35 °C) exhibited an equilibrium adsorption amount of about 22 mg B/g. Furthermore, they stated that, at higher than 50 °C, the content of $\alpha$-D-glucose for PAA-Glu exhibited an increase from the reaction at 35 °C, but the boron adsorption capacity for PAA-Glu exhibited a significant decline.

However, in this study, when PAA-Glu was synthesized at a high temperature (60–100 °C), the $\alpha$-D-glucose content for PAA-Glu exhibited a huge increase, and the boron adsorption capacity and ASA for PAA-Glu showed a considerable improvement.

From our comparison of the adsorbents, we confirmed that the ASA was affected by the adsorbent structure and the location of the hydroxyl groups. As regards the adsorption for boron, commercially available adsorbents (CRB03, CRB05) and PAA-Glu had a lot of unexploited hydroxyl groups for boron adsorption, so we found that there is still room for improvement. We determined through these experiments that the boron adsorption capacity and ASA were improved much more effectively, when the distance between the main chains was controlled appropriately by using a more robust cross-linker, and then the frequency with which boron and adsorption sites collided was increased greatly. We were able to confirm that ASA could be used as a measure of boron adsorbent development.

## 4 Conclusions

We investigated the effect of the PAA-Glu synthesis conditions in relation to boron adsorption. We optimized the amount of added reagents (cross-linker and $\alpha$-D-glucose) and the reaction temperature. PAA-Glu-20-30 adsorbed more boron than the other types of PAA-Glu. However, PAA-Glu-60-30 with the lowest hydroxyl groups exhibited the best ASA value of 46.93 %.

The boron adsorption capacity was obviously smaller than that of other types of PAA-Glu at 130 and 150 °C. At 60–100 °C, the boron adsorption capacity was more than 30 mg B/g. Furthermore, at 60–80 °C, the ASA was more than 35 %. We confirmed that the optimum temperature range of $\alpha$-D-glucose introduction was 60–80 °C for PAA-Glu. We succeeded in selecting the optimum condition for synthesizing PAA-Glu by using adsorption capacity and an index of ASA.

PAA-Glu had a huge advantage as regards increasing the frequency of collisions between boron and hydroxyl groups. However, in the molecular design of an effective boron adsorbent, we found that there remains room for improvement. In this study, we found that the controlling the space between the main chains of a polymer by using a spacer such as a cross-linker allows boron molecules to come and go and leads to an improvement in the boron adsorption amount and ASA. Furthermore, the cost of this adsorbent is estimated to be lower than the cost of commercially available adsorbent because of the inexpensive starting materials and simple synthesis procedure, and this makes our adsorbent a promising candidate replacement for conventional adsorbent.

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