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Boron adsorption mechanism on polyvinyl alcohol

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Abstract Recently, an increase in the use of boron compounds has led to an increase in boron emissions, and concern has grown regarding its detrimental effects on the human body. An adsorbent that adsorbs boron selectively has been developed as a countermeasure. Although certain commercially available boron selective adsorbents can be used to remove boron from aqueous solutions by utilizing the strong affinity between boron and hydroxyl groups, the adsorption capacity appears to be insufficient. So, we adopted polyvinyl alcohol (PVA), which contains many hydroxyl groups, as a model adsorbent. We investigated the boron adsorption characteristics of PVA, and then studied the relationship between the number of adsorption sites and actual adsorption amounts. We assessed the adsorption result by using adsorption site availability (ASA) as an indicator of the ratio of effectively functioning hydroxyl groups from the many hydroxyl groups in PVA. ASA was expressed as a percentage of the experimental equilibrium adsorbed amount in relation to the theoretical equilibrium adsorbed amount. We also compared the adsorption isotherms and ASA obtained with PVA, commercially available *N*-methylglucamine-type resin (CRB03 and CRB05) and the adsorbent we synthesized from polyallylamine (PAA) and glucose (PAA-Glu). Although PVA has many hydroxyl groups in a molecule, ASA analysis revealed that only 6% of the hydroxyl groups in PVA was used for boron adsorption. On the other hand, CRBs and PAA-Glu exhibited higher ASA values (about 15% and 35% respectively) and adsorption amounts, suggesting that the sterically congested adsorbent structure had a great influence on boron adsorption and ASA.

Keywords Boron · Removal · Adsorption · Polyvinyl alcohol (PVA) · Polyallylamine (PAA) · Saccharide

Abbreviations

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

1 Introduction

Boron is an element commonly found in seawater and hot spring water. Boron compounds have a wide range of applications ranging from medicines such as eye drops and gargles to glost and metallic plating in various industries. In recent years, increased boron use has led to increased boron concentrations in wastewater, and concern has grown regarding its detrimental effect on the human body (Parks and Edwards 2005; Nable et al. 1997).

To meet the guidelines for drinking water quality established by the World Health Organization (WHO) (1998), drinking water regulations were strengthened with respect to boron concentration. Subsequently, a number of systems have been developed for removing boron from seawater and wastewater (Inukai et al. 2004; Yasui et al. 2004; Kehal et al. 2008; Oren et al. 2006; Kaby et al. 2008; Yilmaz et al. 2005).

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There are various techniques for removing boron from aqueous solutions, and typical methods include coagulation-sedimentation (del Mar de la Fuente Garcia-Soto and Camacho 2006; Remy et al. 2005), a membrane separation process using reverse osmotic pressure (Qin et al. 2005; Turek et al. 2007), solvent extraction (Matsumoto et al. 1997), evaporation to dryness under reduced pressure (Spicer and Strickland 1958) and adsorption removal using ion-exchange resin, inorganic adsorbent, and organic adsorbent (Yoshimura et al. 1998; Ozturk and Kavak 2008; Kaftan et al. 2005; Sabarudin et al. 2005).

Many adsorbents for the selective removal of boron contain many hydroxyl groups in their molecules and remove boron by utilizing the strong affinity between boron and hydroxyl groups (Labouriau et al. 2006; del Mar de la Fuente Garcia-Soto and Camacho 2005). For the development of boron adsorbents, it might be one of the quickest ways of introducing more hydroxyl groups to increase the amount of adsorbed boron. However, we were confronted with the question of whether boron adsorbents with many hydroxyl groups can always become excellent adsorbents. So, we decided to investigate the relationship between boron and hydroxyl groups qualitatively.

Here we introduce an indicator for assessing the boron adsorption objectively, namely adsorption site availability (ASA). The definition of ASA is as follows;

$$\mathrm{ASA}(\%) = [(\text{equilibrium adsorbed amount from adsorption experiment})/(\text{theoretical equilibrium adsorbed amount})] \times 100. \quad (1)$$

In this paper, we selected polyvinyl alcohol (PVA), which contains many hydroxyl groups, as a model adsorbent. By measuring boron adsorption isotherms for PVA, we calculated ASA for PVA under various adsorption conditions, and compared its value with commercially available *N*-methylglucamine-type resin and our own adsorbent synthesized from polyallylamine (PAA) and glucose.

2 Experiments

2.1 Chemicals

Boron standard solution (1000 mg/l B) was purchased from Merck Co., Ltd. Chlorobenzene (99.5%) and Dimethylamine borane (95%) were purchased from Kishida Chemical Co., Ltd. Ethylene glycol diglycidyl ether (EGDE) was purchased from Tokyo Chemical Industry Co., Ltd. α-D-Glucose was purchased from Sigma-Aldrich. Milli-Q water (Nihon Millipore K.K.) was used to prepare all the solutions.

2.2 Adsorbents

Polyvinyl alcohol (PVA) was purchased from Kishida Chemical Co., Ltd. The degree of polymerization was about 2000 and the degree of saponification was 98.5–99.4 mol%. *N*-Methylglucamine-type resins (DIAION: CRB03, CRB05) were obtained from Mitsubishi Chemical Corporation. Polyallylamine-beads-Glucose (PAA-Glu) was synthesized from poly (allylamine) hydrochloride (PAA) (Mw = 150,000), which was obtained from Nitto Boseki Co.

2.3 Synthesis of Polyallylamine-beads-Glucose (PAA-Glu)

First, Polyallylamine beads (PAA beads) were synthesized as follows: 40.4% w/v aqueous Polyallylamine hydrochloride (PAA-HCl) 70.5 g (containing PAA: 30.3 g, 0.530 mol (-NH_2)) was mixed with 1 mol/L NaOH (256 mL) in a 1 L round-bottomed flask and stirred for 10 minutes at room temperature. A portion of the PAA-HCl solution amine sites was neutralized for crosslinking by adding NaOH. Ethylene glycol diglycidyl ether (EGDE) (7.76 mL, 0.0530 mol) was added to the solution and stirred vigorously for 2.5 minutes. The reaction solution was poured into chlorobenzene (700 mL) immediately, before it turned completely into a gel, and then stirred continuously for 12 hours at room temperature. The solution was filtered and evaporated to remove as much chlorobenzene as possible. The subsequent reaction used PAA beads (20% cross-linked) without the need to dry them (Zeng and Ruckenstein 1998; Ngah et al. 2002).

Next, Polyallylamine-beads-Glucose (PAA-Glu) was prepared according to the following procedure reported by Kaida et al. (2002, 2003). α-D-Glucose (76.4 g, 0.424 mol) was dissolved completely in 400mL of H_2O, and this solution was then added to the PAA beads (20% cross-linked) suspended in solution and stirred. Then, the suspension was added to dimethylamine borane (25.0 g, 0.424 mol) and stirred continuously for 24 hours at 303 K. 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 (72.0 g) was obtained.

In this study, the main target was the assessment of PVA, and so a long-chain polymer 'polyallylamine' was selected as a compound with a similar structure to that of PVA. We made a simple comparison between PVA and PAA-Glu. In the insoluble treatment of PAA by cross-linking, PAA gel beads were formed when EGDE equivalent to 20% with respect to the total number of amino groups was added to the

PAA solution. It is important to research the impact on the additive amount of EGDE. However, in this study, because it was important to compare the results with the boron adsorption characteristics of PVA, we did not investigate the optimum amount of EGDG addition.

2.4 Estimation of number of hydroxyl groups

The number of hydroxyl groups was estimated from the composition formula for PVA, CRB03, CRB05 and PAA-Glu. The estimation procedure was as follows: PVA: PVA ($n = 2000$) with an average molecular weight of 88,000 has 2000 units (-OH) in one molecule. The number of hydroxyl groups for PVA was estimated from the molecular weight and polymerization degree.

The chemical compositions of CRB03, CRB05 and PAA-Glu were confirmed with a CE Instruments EA1110 elemental analyzer.

CRB03 and CRB05: The chemical structural formula of the CRBs was provided, however, their elemental content was not given in detail. So, from an elemental analysis, we assumed that the entire nitrogen content of the CRBs originated from *N*-methylglucamine group and the nitrogen number was equivalent to the number of functional groups. The number of hydroxyl groups for the CRBs was estimated from the number of *N*-methylglucamine groups with 5 hydroxyl groups in one molecule.

PAA-Glu: The carbon and nitrogen content of the PAA beads and PAA-Glu was obtained from an elemental analysis. In these synthesized compounds, the amount of nitrogen atom in PAA does not change by the introduction of glucose. So, as a reference to the nitrogen content, the difference in the carbon content between the PAA beads and PAA-Glu was calculated from the analysis data. We assumed that the increased amount was equivalent to the amount of introduced glucose with 5 hydroxyl groups in one molecule. We express the carbon and nitrogen content of the PAA beads and PAA-Glu as follows: C_{beads}, N_{beads}, C_{Glu} and N_{Glu}. The number of hydroxyl groups was calculated using the following formula:

$$\text{The number of hydroxyl groups (unit/g)} = \{[C_{Glu} - (C_{beads} \times N_{Glu}/N_{beads})] \times 5 \times N_A\} / (100 \times 12.011 \times 6) \quad (2)$$

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.

2.5 Adsorption experiment

Diluted boron solutions containing 250, 125, 62.5 and 31.25 ppm were prepared from boron standard solution (1000 ppm) at pH 2–13, and then these solutions were assumed to be simulated boron wastewater. Given amounts of adsorbents (0.0200–1.25 g) were added to the boron solutions (10 mL or 50 mL) and stirred at 120 rpm at 298 K. Batch adsorption experiments were carried out that lasted 3 hours for PVA and 24 hours for CRB03, CRB05 and PAA-Glu. 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).

3 Results and discussion

3.1 Synthesis of PAA-Glu

Since PAA-gel beads are not currently commercially available, we first synthesized PAA-gel beads and then modified them with α-D-glucose. Although PAA-gel beads modified with saccharide have already been reported, there has been no detailed study of the influence of the reaction conditions on the formation of PAA gel modified with sugars. A diagram of the PAA-Glu synthesis technique is shown in Fig. 1.

Before modifying the PAA-gel with α-D-glucose, we prepared water insolubilized PAA-gel beads by cross-linking because PAA-gel is water soluble and unsuitable for adsorption measurements in aqueous solution. Water-insoluble PAA-gel beads were synthesized from PAA with EGDE. The obtained PAA-gel beads were macroscopic particles after drying. Then α-D-glucose was introduced into the PAA gel via a reductive alkylation between the PAA-gel beads and glucose using the procedure reported by Kaida et al. (Kaida et al. 2002; Kaida et al. 2003). The C/N ratio of the PAA beads and PAA-Glu was obtained from the elemental analysis as shown in Table 1.

3.2 Boron adsorption on PVA

We selected polyvinyl alcohol (PVA) containing many hydroxyl groups as a model adsorbent and investigated the boron adsorption properties.

First, we investigated the influence of pH on the adsorption isotherms using boron solutions with different pH values, and the corresponding boron adsorption isotherms are shown in Fig. 2.

Table 1 The results of the elemental analysis for PAA beads, PAA-Glu, CRB03 and CRB05

Sample	C (%)	N (%)	C/N
PAA beads	36.4252	10.4956	3.4705
PAA-Glu	40.0537	5.6173	7.1304
CRB03	67.0179	3.5926	18.6547
CRB05	65.7399	3.6516	18.0033

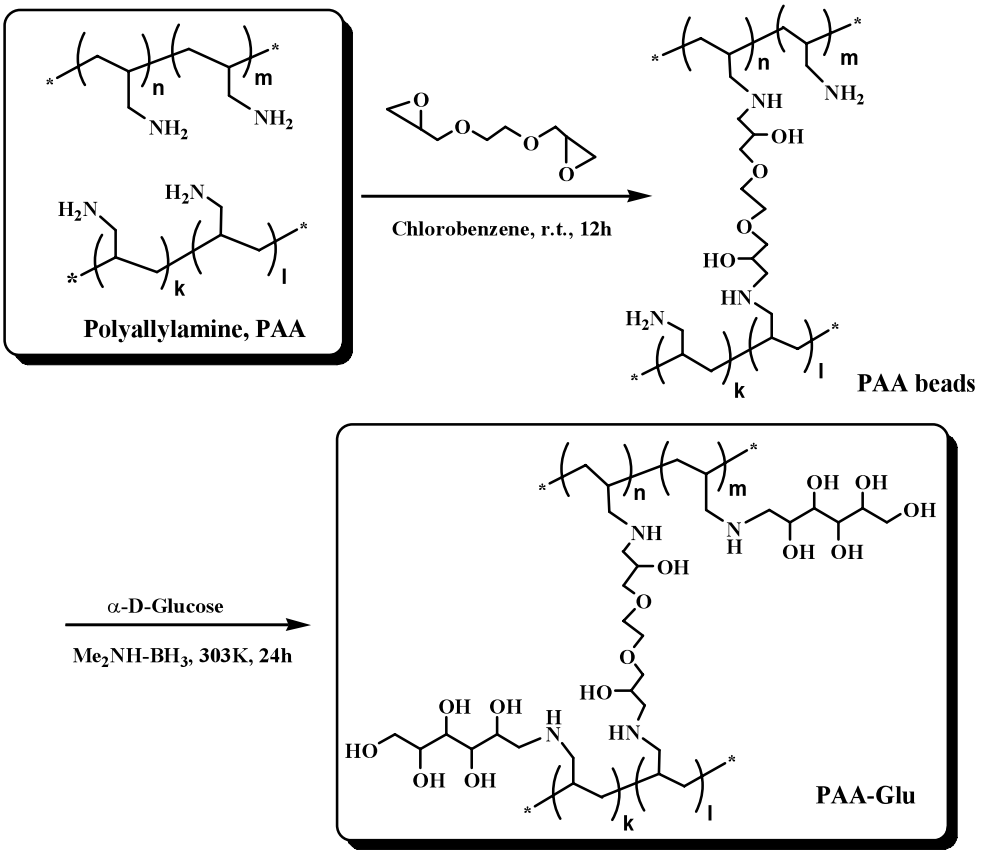

Fig. 1 Cross-linkage of Polyallylamine and introduction of α-D-Glucose

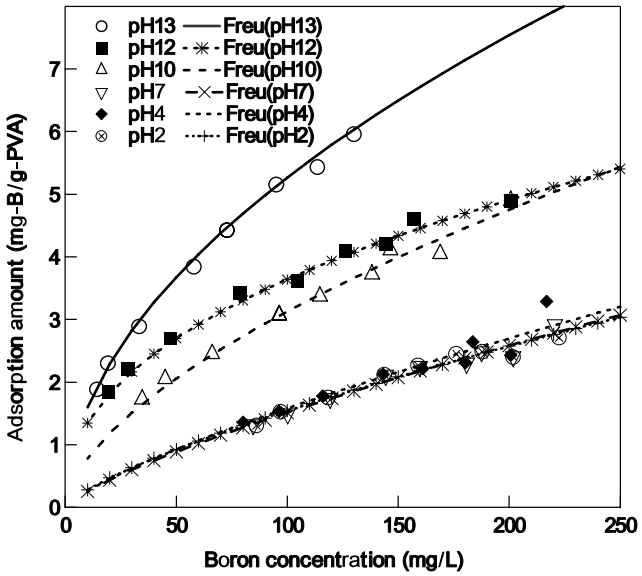

Fig. 2 Adsorption isotherms for PVA ($n = 2000$) and boron simulated wastewater (250 ppm-boron, pH2-13)

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

$$q = k_f C^{1/n} \tag{3}$$

where q is the adsorption amount (mg/g), k_f is the adsorption constant, C is the boron concentration (mg/L) and $1/n$ is an arbitrary parameter. The relationship between the adsorption constant (k_f) and the pH for different boron concentrations (31.25–250 ppm,) is shown in Table 2. The reason for selecting the Freundlich equation rather than the Langmuir equation is mentioned later.

The adsorption amount under basic conditions was much larger than that under acidic conditions. The reason for this difference can be explained as follows. We believe that the adsorption was mainly caused by the affinity between tetrahydroxyboric acid anions and hydroxyl groups (Labouriau et al. 2006; del Mar de la Fuente Garcia-Soto and Camacho 2005). Boron species exist mainly as tetrahydroxyboric acid anions under basic conditions and as boric acid under acidic conditions. Therefore the adsorption under basic conditions is more favorable than under acidic conditions. The optimum pH range for boron adsorption on PVA was around 13 from Fig. 2.

3.3 Comparative discussion of other adsorbents

To check the optimum pH range for CRB03, CRB05 and PAA-Glu, the boron adsorption amount was compared for a constant amount of each adsorbent as shown in Fig. 3. The optimum pH ranges were 5–7 for CRB03, CRB05 and 8–9

Table 2 Freundlich constants of boron adsorption onto PVA ($n = 2000$) [boron solution (31.25–250 ppm, pH2-13)]

pH	250 ppm[a]		125 ppm[a]		62.5 ppm[a]		31.25 ppm[a]	
	k_f[L/g]	$1/n$ [–]	k_f[L/g]	$1/n$ [–]	k_f[L/g]	$1/n$ [–]	k_f[L/g]	$1/n$ [–]
2	0.0515	0.7383	0.1206	0.4823	0.0602	0.6135	0.0404	0.9646
4	0.0456	0.7701	0.0930	0.5607	0.0614	0.6035	0.0434	0.6683
7	0.0433	0.7718	0.0909	0.5585	0.0944	0.4714	0.0501	0.6026
10	0.1941	0.6035	0.2369	0.5245	0.1958	0.5650	0.2282	0.4954
12	0.4989	0.4315	0.4310	0.4430	0.4190	0.4197	0.2434	0.5998
13	0.4855	0.5176	0.3463	0.6179	0.3030	0.6588	0.1865	0.7921

[a]250–31.25 ppm: initial concentration of boron solution [ppm (mg-B/L)]

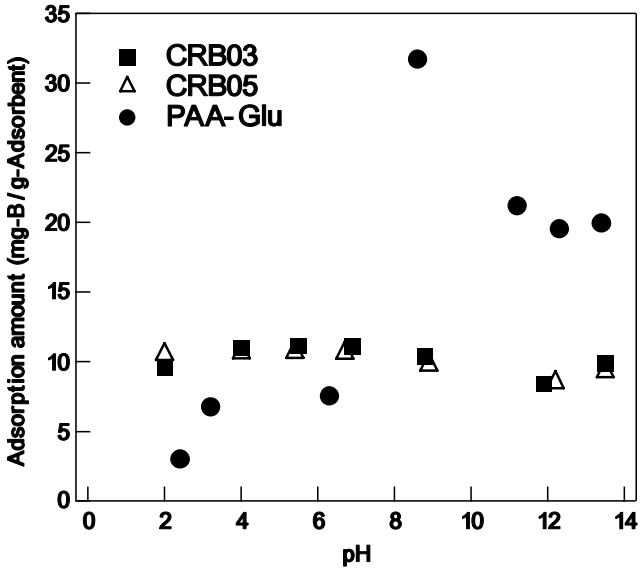

Fig. 3 Boron adsorption amount for CRB03 (200 mg), CRB05 (200 mg) and PAA-Glu (50 mg) in each type of boron simulated wastewater

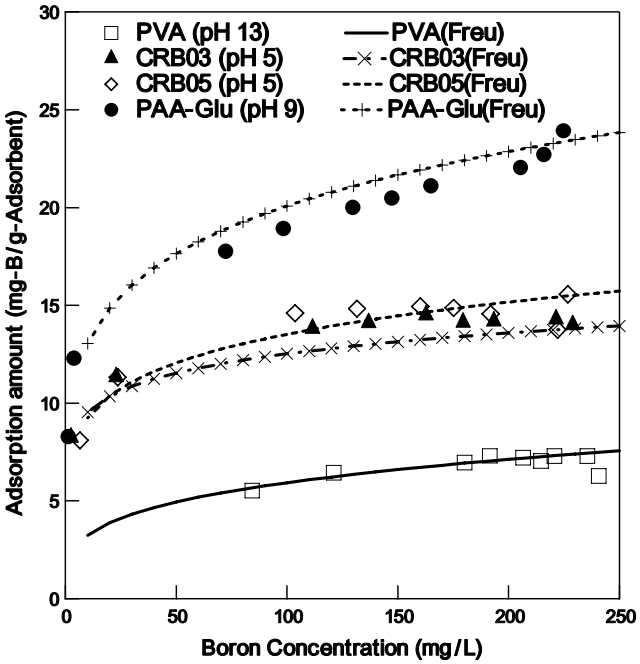

Fig. 4 Boron adsorption isotherm and Freundlich isotherm for PVA, CRB03, CRB05 and PAA-Glu

for PAA-Glu. All of the adsorption measurements described below were carried out in the optimum pH range for each adsorbent.

Boron adsorption isotherms for CRB03, CRB05, PAA-Glu and PVA are shown in Fig. 4. All of the isotherms were analyzed using the Freundlich equation and the fitted parameters are listed in Table 3. The adsorption constant (k_f) for CRB03, CRB05, and PAA-Glu exhibited a much larger value than that of PVA, whereas there was much less difference between the ($1/n$) values. Therefore, the main reason for the larger adsorption amount for CRB03, CRB05 and PAA-Glu is not the difference between the affinities of the adsorption site (glucamine and hydroxyl group) and the boron species. For PVA, CRB03 and CRB05, both the Langmuir equation and the Freundlich equation provided a good fitting. However, the Freundlich equation provided a better fitting than the Langmuir equation for PAA-Glu. Therefore, in this paper, we adopted the Freundlich equation for analyzing the boron adsorption isotherm from PVA, CRB03, CRB05 and PAA-Glu in just one method.

Table 3 Freundlich constants of boron adsorption onto PVA, CRB03, CRB05 and PAA-Glu

Adsorbent	Freundlich constants		Correlation coefficient, R^2
	k_f [(L/g]	$1/n$ [–]	
PVA ($n = 2000$)	1.7660	0.2633	0.9414
CRB03	7.2678	0.1182	0.9587
CRB05	6.3308	0.1649	0.9154
PAA-Glu	8.4902	0.1870	0.9484

We estimated the theoretical number of hydroxyl groups for each adsorbent based on Sect. 2.4. The C/N ratios of PAA beads, PAA-Glu, CRB03 and CRB05 were obtained from the elemental analysis as shown in Table 1. The calculated number of hydroxyl groups for each adsorbent listed in the third column of Table 4.

Table 4 Adsorption site availability (ASA) for adsorbents

Adsorbent	pH	The number of hydroxyl groups (unit/g)	Theoretical equilibrium adsorbed amount (mg-B/g-adsorbent)	Experimental equilibrium adsorbed amount (mg-B/g-adsorbent)	ASA[a] (%)
PVA($n = 2000$)	13	13.68×10^{21}	122.9	7.5	6.1
CRB03	5	7.72×10^{21}	69.3	13.1	18.9
CRB05	5	7.85×10^{21}	70.5	13.9	19.7
PAA-Glu	9	8.59×10^{21}	77.1	26.7	34.6

[a]ASA: Adsorption site availability

The measurement in the elemental analysis was very sensitive and was affected by organic solvents included in the samples. Particularly close attention was paid to washing and drying the adsorbents in this work. We noted changes of the contained amounts for carbon and nitrogen to investigate the progress in each reaction. Even if the adsorbents contained a small amount of water, their C/N ratio was unaffected. The error for measurements of the same sample in the elemental analysis result was within 3%.

To explain the difference in the adsorption amount, we employed adsorption site availability (ASA), which we define as follows,

$$\mathrm{ASA}(\%) = [(\text{equilibrium adsorbed amount from adsorption experiment})/(\text{theoretical equilibrium adsorbed amount})] \times 100.$$

We calculated this ASA for the examined adsorbents. Using the ASA, we can compare adsorption sites within adsorbents and the actual number of adsorption sites that utilized boron adsorption. In this comparison of adsorption sites, we assumed that boron adsorption was induced between a tetrahydroxyboric acid anion and a hydroxyl group, so we performed a calculation solely for the hydroxyl group. For simplicity, we only considered the hydroxyl group as the adsorption site and we ignored the effect of nitrogen atoms.

Many researchers have adopted a combination pattern where one boron molecule is combined with two hydroxyl groups in their work on boron adsorption. The combination style of the boron-hydroxyl group is shown in Fig. 5. Meanwhile, the combination between the boron and hydroxyl groups adopted various conformation patterns including bisether, tetraether or another ether formation. The possible PVA's conformation pattern is shown in Fig. 6 (Sinton 1987; Maerker and Sinton 1986). These conformations depend on the boron concentration, pH and other factors.

However, the only thing we know about the boron-hydroxyl group combination is that at least one boron molecule combined with two hydroxyl groups. So, we adopted a minimum consumption level of 'two hydroxyl groups'. So, we calculated the theoretical saturated adsorption amount

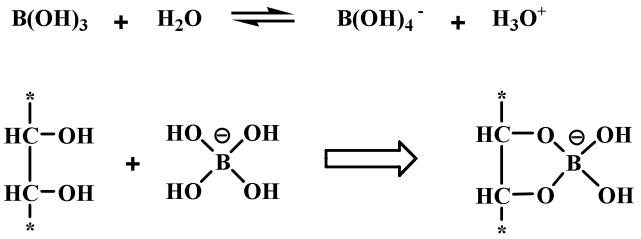

Fig. 5 Disconnection of boric acid and boron adsorption to adsorbent

assuming that one boron molecule combined with two hydroxyl groups. The ASA for each adsorbent is shown in Table 4.

As described above, the affinity between boron and the adsorption site in the four adsorbents were in the same range. Nevertheless, PVA, which contained the most hydroxyl groups per unit weight, exhibited a smaller adsorption amount and ASA than the other three adsorbents. Meanwhile, adsorbents with a saccharide, such as CRB03, CRB05 and PAA-Glu exhibited about 2–4 times the adsorption amount and about 3–6 times the ASA compared with those of PVA.

It is reasonable to suppose that boron adsorption was affected by the steric conformation of the hydroxyl groups on the adsorbent. In the same way as a polymer, PVA has a folded straight chain, which provides the compound with energy stability and then adopts a densely packed form (Wolf and Suter 1984). We considered that hydroxyl groups directly coupled to the PVA chain were located internally in a sterically tangled structure. As the adsorption progressed, the binding with boron became increasingly difficult. The PVA surface was coated with boron immediately after the adsorption started, and so the internal hydroxyl groups were completely incapable of participating in the boron adsorption. Furthermore, when a single molecule of boron formed a bond with two hydroxyl groups, the bond formation was difficult to promote because of the large bond distance between the two hydroxyl groups. Either way, many of the hydroxyl groups in a molecule were not effectively used for binding to boron, and it was easy to deduce that the sterically tangled PVA structure had a great influence on boron adsorption.

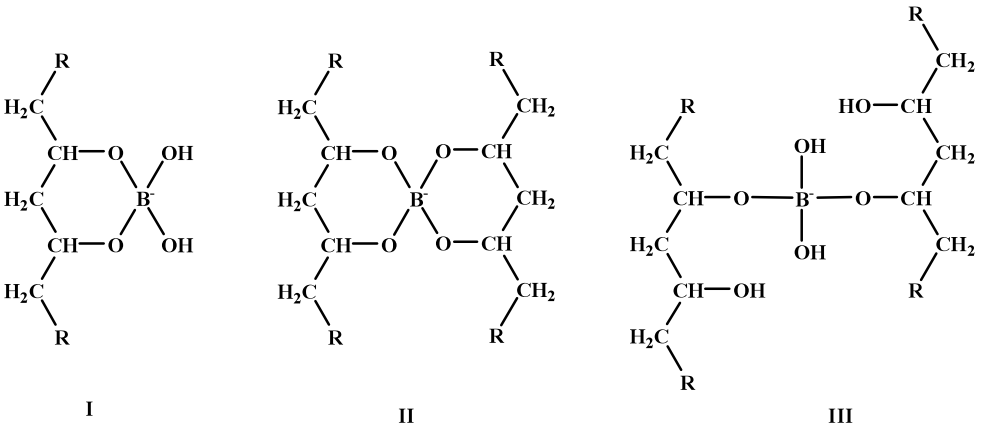

Fig. 6 The conformation patterns of combinations of boron and PVA (I: Bisether, II: Tetraether, III: Intermolecular bisether)

On the other hand, the ASA values and boron adsorption amount for CRB03 and CRB05 were higher than the results for PVA. They had a huge advantage as regards increasing the frequency of collisions between boron and hydroxyl groups because the hydroxyl groups were located at a point distant from the main chain of the compound and had a lot of flexibility. However, in the molecular design of an effective boron adsorbent, we found that there is still room for improvement. PAA-Glu exhibited an equilibrium adsorption amount of about 27 mg-B/g and an ASA of about 35% and produced a considerable improvement. The ASA values and boron adsorption amount for PAA-Glu were better than for the other three adsorbents, but the values were not always sufficient.

From these results, we were able to confirm that ASA could be used as a measure of boron adsorbent development. We found that it was more important to introduce a number of hydroxyl groups into an adsorbent location that boron could access easily. So, in the future development of adsorbents, it will be an even more important challenge to develop an adsorbent with a high ASA value and adsorptive capacity.

4 Conclusions

In this study, we revealed the relationship between the actual adsorption amount and the adsorption site by using an index of the adsorption site availability (ASA). From an analysis of adsorption isotherms, the affinity between boron and an adsorption site (purely focusing on hydroxyl groups) was in the same range for any of the adsorbents. Therefore, we found that a sterically congested adsorbent structure had a great influence on boron adsorption.

From these results, the ASA values and boron adsorption amount were very low for PVA. PVA had the most number of hydroxyl groups of the four adsorbents, but it was insufficient for effective boron removal. In addition, it should to be noted that commercially available adsorbents, even CRB03 and CRB05, exhibited an equilibrium adsorption amount of about 13 mg-B/g and an ASA of less than 20%.

For this reason, we found that even these commercially available adsorbents had a considerable number of unexploited adsorption sites, and this suggests that there is significant scope for the further improvement of boron selective adsorbents. We succeeded in verifying the hypothesis that the improvement in the adsorption amount realized by PAA-Glu resulted from the fact that the synthesized adsorbent had a structure where a hydroxyl group bound to an alkyl chain of PVA seemed to be replaced by saccharide that became a hydroxyl group with a high degree of freedom. This improved the adsorption ability of the adsorbent.

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