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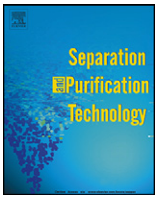

Short communication

The rapid boron uptake by multi-hydroxyl functional hairy polymers

Mustafa Gazi[a], Giancarlo Galli[b], Niyazi Bicak[a,*]

[a] *Istanbul Technical University, Chemistry Department, Maslak 34469, Istanbul, Turkey*
[b] *University of Pisa, Dipartimento Chimica & Chimica Industriale, I-56126 Pisa, Italy*

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ABSTRACT

A novel functional polymer resin with extremely rapid and selective boron sorption ability is reported. Thus, 2-hydroxyethylamino 2,3-propanediol was introduced to dangling poly(glycidyl methacrylate) graft chains on crosslinked poly(styrene-divinyl benzene) (PS-DVB) microspheres (210–420 μm), by ring opening of the oxirane units involved. The resulting hairy polymer with multi-hydroxyalkylamine functions on the graft chains was demonstrated to bind boric acid (3.28 mmol g^{-1}) selectively; similar to ordinary bead polymers with the same chelating units tethered directly to the particle surfaces. Significant difference was unusually rapid boron uptake ability of this new polymer material, due to partial mobility of the dangling grafts carrying the boron chelating ligands. Batch kinetic experiments showed that, 1 g of the polymer sample is able to remove trace boron (100 ppm) from 100 mL aqueous solution (non-buffered) within contact-times less than 2 min. This is very short time comparing with those of ordinary functional bead polymers (i.e. 30 min). Also regeneration of the boron loaded resin by acid treatment was shown to be reasonably fast. Effect of pH, presence of some foreign ions on the boron sorption and regenerability of the polymer were investigated and compared with those of the ordinary functional bead polymers.

1. Introduction

Removal of trace boron from water is of special importance due to its plant stunting effect. Adsorption on inorganic pigments such as magnesium hydroxide has been demonstrated to show limited success in removal of boron [1]. Recently Itakura et al. [2] described a process in which more than 99% of boric acid is removed by sorption with $Ca(OH)_2$ at high temperatures (150 °C), in the presence of H_3PO_4.

Strong base anion-exchange resins have been found effective for boron removal, but all other ionic species are also removed, rendering the operation uneconomical especially when the boron concentration is high [3].

Polymers with multi *vicinal*-diol functions such as sorbitol [4] and mannitol are able to bind boric acid specifically by forming stable boron esters even in aqueous solutions. Based on this chemistry a boron-specific commercial resin, Amberlite IRA-743 with *N*-methyl D-glucamine functional groups emerged in the 1960s [5]. This resin is highly specific and able to reduce boron concentration to below 1 ppm [6]. However, expensive resin regeneration and capacity loss in each regeneration step make the process unsatisfactory [7].

Recently we demonstrated that selective boron uptake is not confined to sugar derivatives. Imino bis-propyleneglycol [8] and 2-hydroxyethylamino-2,3-propanediol functions [9] are also very efficient in selective boron binding. Crosslinked bead polymers having those chelating groups are able to remove trace boron and show no activity loss after 20 times of recycling. Following studies of Smith et al. revealed that branched polyethyleneimines modified with suitable epoxy compounds are also efficient in sorption of trace boron and the boron chelation considerably increases by increasing number of hydroxyl groups around the amine nitrogen [10].

Despite their high selectivity and regenerability, those materials are somewhat slow especially in removal of trace boron due to heterogeneity of the process. For instance, to reduce the boron concentration around 1 ppm, the aqueous solution must be contacted with the resin material for 30 min or longer [11,12].

It is envisaged that this period may be shortened considerably if surface grafts on the crosslinked bead core are employed as carriers for boron chelating groups. Topologically these materials would be quite different from conventional polymer resins in which the functional groups are located on the solid particle surfaces. In such a structure, the chelating groups are placed on the flexible graft chains, and their partial mobility in the liquid phase would make the functional groups faster in chelating with H_3BO_3. In another words the flexibility of the chains are expected to provide nearly homogenous reaction conditions and faster reaction rates as well.

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* Corresponding author. Tel.: +90 212 285 3221; fax: +90 212 285 6386.
E-mail addresses: gazi@emu.edu.tr (M. Gazi), gallig@dcci.unipi.it (G. Galli), bicak@itu.edu.tr (N. Bicak).

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In order to prove this assumption, in the present work, poly(styrene-divinyl benzene) (PS-DVB) microspheres having poly(glycidyl methacrylate) surface grafts were prepared onto which 2-hydroxyethylamino-2,3-propanediol functions were then incorporated as boron chelating units. Boron uptake efficiency of the polymer, effect of foreign ions and regeneration conditions were investigated, with a main focus on the boron sorption kinetics. The results were compared with those of the PS-DVB resin beads carrying the same boron chelating groups directly tethered onto their surfaces.

2. Materials and methods

All the chemicals used were analytical grade: Styrene (E. Merck) and divinyl benzene (E. Merck) were rendered inhibitor free by washing with NaOH solution (3%) prior to use. CuBr was freshly prepared according to the procedure described in the literature [13]. The atom transfer radical polymerization (ATRP) ligand, H-TETA (1,1,4,7,10,10-hexakishexyl-1,4,7,10-tetraazadecane) was prepared by alkylation of triethylene tetramine with 1-bromohexane as described earlier [14]. Glycidyl methacrylate (GMA) (Aldrich) was distilled before use. Ethanolamine (Merck) and glycidol (Acros Organics) were purified by distillation under vacuum. Chlorosulfonic acid (Aldrich), propylamine (Aldrich), and all the other chemicals were analytical grade products and were used as purchased.

2.1. Preparation of PS-DVB resin beads with poly(glycidyl methacrylate) (PGMA) surface grafts

This was performed by surface initiated graft copolymerization of GMA from bromosulfonamide groups on PS-DVB resin beads, using CuBr complex of H-TETA as ATRP catalyst, as described previously [15]. Thus, 7 g of the starting resin with 1.26 mmol g^{-1} of bromosulfonamide density gave 26.9 g of graft product with 5.41 mmol g^{-1} of epoxy group density, as assayed by pyridine–HCl method [16]. Considering with mass increase (284.3%) and replaced bromine (1.26 mmol g$^{-1)}$ the grafting per gram of non-brominated sulfonamide resin will be $2.843 + 80 \times 1.26 \times 10^{-3} = 2.9438$ g. This corresponds to a 294% grafting.

2.2. Preparation of 1-(2-hydroxylethylamino)-2,3-propanediol (HEP)

This was prepared by the reaction of redistilled glycidol (32.8 mL, 0.5 mol) with excess ethanolamine (107 g, 1.5 mol), as described before [9]. Its purity was checked by thin layer chromatography (TLC) and ^{1}H NMR. The colorless viscous liquid so obtained was pure enough for the next reaction (yield 77%).

2.3. Modification of the PGMA grafts with HEP

5 g of the bead polymer was added portion-wise to the stirred solution of 5 g HEP in 10 mL of 1,4-dioxane at room temperature. The mixture was placed on a continuous shaker and shaken for 24 h at room temperature, then heated to 70 °C for 60 min, filtered and washed with 250 mL of water. The product was transferred into a beaker with 250 mL water and left in contact overnight. The filtered product was washed several times with water (5× 200 mL), ethanol (15 mL), ether (10 mL) and dried under vacuum at 45 °C for 48 h. The dry product weighed 7.2 g.

Conversion of the epoxy groups of the GMA component was assessed by determination of amine content of the modified resin, as follows: 0.5 g of the above product was stirred with 10 mL of 1 M HCl solution for 24 h at room temperature. The mixture was filtered and unreacted acid content was determined by titration of 5 mL of the filtrate with 0.1 M NaOH (factor of the solution, $F = 1.0395$) solution in the presence of phenolphthalein color indicator. Thus 5.2 mL of the NaOH consumption against the blank indicated a 3.28 mmol g^{-1} of total amine content.

2.4. Determination of the boron loading capacity

Boron loading capacity of the resin was determined by interaction of 0.25 g of the polymer sample with artificial boric acid solution in non-buffered conditions. The sample was wetted with 5 mL of distilled water for 15 min to 9 h. Three grams of H_3BO_3 (4.852×10^{-2} mol) was dissolved in water and diluted to 100 mL. 25 mL of this solution was added to the above mixture and the mixture was shaken on a shaker for 15, 30, 60, 120, and 3600 min at room temperature. The mixtures were filtered and the residual boron contents of the respective solutions were determined by titration of 2 mL of the filtrate in the presence of 10 mL of 0.5 M sorbitol solution using phenolphthalein as color indicator, as described in the literature [17]. Thus, consumption of 15.1 mL of 0.05 M NaOH ($F = 0.99784$) (16.2 mL for the blank) indicated a H_3BO_3 loading capacity of 3.29 ± 0.02 mmol per gram of polymer.

In order to inspect effects of foreign ions, the capacity measurements were repeated in the presence of Ca(II), Mg(II) and Fe(III). The solutions were prepared from binary mixtures of H_3BO_3 with $CaCl_2$, $MgSO_4 \cdot 7H_2O$ or $Fe(NO_3)_3 \cdot 9H_2O$, so that the final concentration of the foreign ions was 0.14 M, while keeping the boron concentration constant at 0.41 M. Non-absorbed boric acid and the metal ions were assayed separately by analysis of each component. Ca(II), Mg(II) and Fe(III) ions were determined by titration with a solution (0.1 M) of the disodium salt of ethylenediamine tetraacetic acid (EDTA). In order to avoid probable interferences of the foreign ions, the boric acid concentrations in this case were assigned colorimetrically ($\lambda = 585$ nm) by carminic acid method [18]. These experiments were repeated also in the absence of boric acid to determine the extractability of the foreign ions alone.

Effect of pH on boron sorption was also studied by using buffered solutions of H_3BO_3. For this purpose a series of buffer solutions was prepared (100 mL of each) by using appropriate combinations of 0.2 M sodium acetate and 0.2 M acetic acid solutions for pH 2, 4.05, and 5 and 0.06 M sodium hydrogen phosphate and 0.06 M potassium dihydrogen phosphate for pH 8. In each buffer solution, 1.5 g (24.3 mmol) of H_3BO_3 was dissolved and made up to 50 mL, so that the final concentration was 0.485 M. These solutions were stirred with the polymer samples (0.25 g of each) for 4 h at room temperature. The boron uptakes were assayed similarly.

2.5. Desorption of boron from loaded samples

Acid leaching method was employed for desorption of the boron as follows: loaded resin sample (0.25 g) was left in contact with 5 mL of water for 30 min to 24 h. Then 20 mL of 4 M HCl solution was added and stirred at room temperature. In order to inspect the desorption rates; the samples (2 mL) were withdrawn after stirring for 10, 30, 60, and 120 min. The aliquots were filtered and the hydrochloric acid excess was titrated with 0.05 M KOH solution in the presence of phenolphthalein indicator. At the end points of neutralization, 10 mL of 0.5 M D-sorbitol solution was added to the mixtures and titrations with KOH solution were continued until reappearance of the pink color. Desorbed amounts of boron were calculated from the base consumptions in the second stages.

After the acid treatment the polymer samples were filtered, washed with 20 mL of 0.1 M NaOH solution and excess of distilled of water (3× 50 mL). Boron-free polymer samples so obtained were reusable.

3. Results and discussion

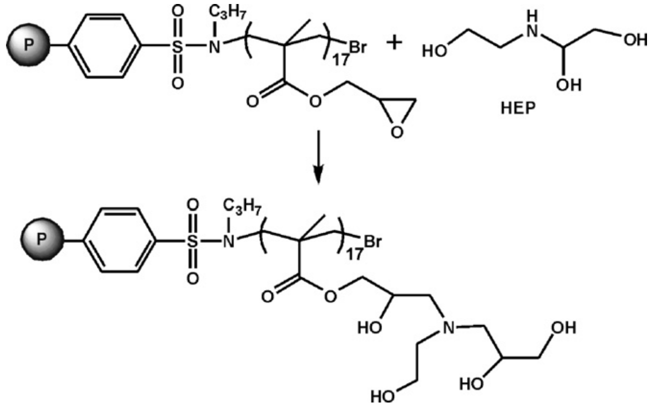
3.1. Synthesis of the boron chelating resin

The base polymer resin (PS-DVB)-*graft*-PGMA was prepared by ATRP of GMA from *N*-bromosulfonamide initiator groups on PS-DVB microspheres (210–420 μm) as described before [15].

Design of such polymer architectures with surface tethered functional grafts was almost impossible in the past. Fortunately new emerged controlled/living radical polymerization techniques have made it possible. Copper mediated atom transfer radical polymerization (ATRP) has shown to be especially useful for graft copolymerization of various monomers from solid surfaces [19,20]. ATRP is superior to other techniques in surface initiated graft copolymerization, since only negligible quantities of free-homopolymers form as by-products [21]. Incorporation of the halo-alkyl initiation sites to the solid surface is the most crucial step for success of the grafting process. One common route to creating initiator groups is surface modification of hydroxyl containing bead polymers by esterification with 2-bromo isobutyryl bromide [22]. Chloromethyl groups of commercial Merrifield resin have also been employed as surface initiator for graft copolymerization with *N*,*N*-dimethyl acrylamide, but found to be less efficient comparing with bromoalkyl functions [23]. Hydroxyethyl groups supported onto PS-DVB have been esterified similarly with 2-bromoisobutyryl bromide and the resulting material has been employed as a solid macro-initiator for preparing block-graft copolymers including poly(MMA-*co*-GMA), poly(MMA-*co*-dimethylaminoethyl methacrylate) tethered to solid particle surfaces [24]. However, hydrolytic instability of the ester linkages connecting the graft chains with the solid surface does not allow modification of those graft chains for further functionalization. To overcome this drawback, we have recently developed the atom transfer graft copolymerization of GMA from surface bound *N*-bromosulfonamide groups yielding surface grafts connected by hydrolytically stable sulfonamide bonds [15].

The epoxy content of the (PS-DVB)-*graft*-PGMA resin was 5.41 mmol g^{-1} (by pyridine–HCl method) indicating an average 17 repeating GMA units per initiation site. Modification of the PGMA graft chains by reacting with excess of 2-hydroxyethylamino-2,3-propanediol (HEP) led to a boron chelating polymer as depicted in Scheme 1.

3.2 mmol g^{-1} of amine content of the chelating polymer (by acid titration) revealed almost quantitative functionalization of the oxirane groups on the PGMA side chains. In the FT-IR spectra of the base polymer (Fig. 1a) a broadened band at 1150 cm^{-1} is associated with the —C—O— stretching vibration band of oxirane group. After modification with HEP (Fig. 1b) a new intense band appears at 1050 cm^{-1} which is assigned to the —C—O— stretching vibration of the ring-opened ether linkage. A broad band at 3200–3400 cm^{-1} is due to the stretching vibration of —OH groups of the chelating units introduced. The typical carbonyl group vibration band of methacrylate unit remains unchanged at 1725 cm^{-1}.



Scheme 1. Preparation of the boron chelating resin by modification of PGMA graft chains on PS-DVB microspheres with HEP.

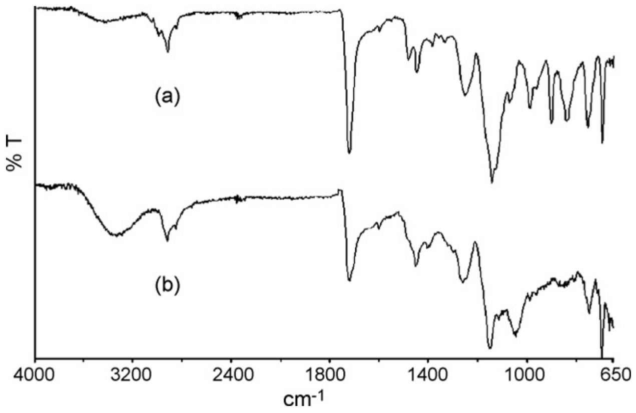


Fig. 1. FT-IR spectra of the pristine poly(GMA) grafted resin (a) and after modification with 2-hydroxyethylamino functional groups (b).

3.2. Boron chelation

The resulting resin showed interesting boron chelating behavior which is quite different from those of the resins possessing the same chelating functions tethered directly to surface of the microspheres [9]. Boron loading capacity of wetted resin was determined to be 3.29 ± 0.01 mmol g^{-1} in non-buffered conditions. This amount is almost equal to the content of 2-hydroxyethylamino-2,3-propanediol groups (3.28 mmol g^{-1}) indicating a hundred percent efficiency of the chelating functions.

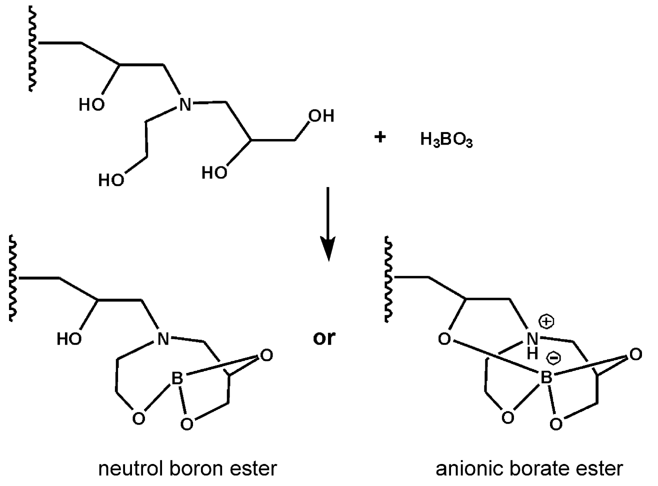
Moreover time length for maximum loading of this resin was shown to be reasonably short. Although we have not studied for shorter loading times, the capacities measured within 15–3600 min were close to each other (see Table 1). This table implies that 30–35 min of contact time is enough to attain maximum boron sorption capacity and practically boron uptake remains almost constant beyond that.

This unusual behavior must be due to flexibility of the graft chains carrying the chelating groups which promotes very effective and fast chelation. The chemical structure of the boron chelating unit is one other important factor for rapid boron uptake in very short times. The present boron chelating ligand contains four hydroxyl groups which are sufficient to hold up one boric acid molecule by forming either neutral boron ester or anionic borate ester (Scheme 2).

Table 1
Boron uptake from H_3BO_3 solution (4.852 × 10^{-3} M) at various contact times

Stirring time (min)	Boron loading[a] (mmol g^{-1})
15	3.19 ± 0.02
30	3.23 ± 0.02
60	3.29 ± 0.02
120	3.28 ± 0.01
3600	3.28 ± 0.01

[a] 1 g polymer per 100 mL solution.



Scheme 2. Possible chelation of boric acid with HEP function attached to the graft chains.

Therefore, each pendant unit constituting with one amine nitrogen and four hydroxyethyl groups behaves as individual chelating ligand and chelating with boron does not require additional hydroxyl groups from the neighbor chains. In other words complexation with boric acid does not result in crosslinking between the graft chains. Overall result is full occupation of the chelating groups and rapid boron uptake, as if the reaction took place in homogenous medium.

We have also tried to follow boron uptake kinetics by batch method using highly diluted boric acid solution (100 ppm, 9.24×10^{-3} M). However, we were not able to follow the kinetics since no detectible boron remained in 100 mL solution after 2 min of stirring with 1 g of the chelating polymer. This result clearly indicates unusual rapid boron uptake ability of the polymer even from dilute solutions. Whereas for the case of microspheres carrying the same chelating units the time length to reduce boron concentration below 1 ppm is around 30 min [9] in the same batch reaction conditions.

Similar behavior was observed in recovery of boric acid from loaded resin by leaching with 4 M HCl solution. It was shown that 3.2 mmol boric acid is released by stirring the loaded sample (1 g) with acid for 30 min (Table 2). This quantity accounts for about 98% of the capacity. However, based on boron-free polymer this amount is almost equal to capacity of the resin. This implies that boron stripping by acid treatment is also fast and completed within 30–35 min, as in the case for loading.

After stripping of boron by acid treatment, tertiary amino groups of the ligating units become protonated. The free amine form is restored by washing with dilute NaOH solution (0.1 M) and the chelating polymer becomes regenerated.

Boron uptake capacity of the regenerated polymer sample was also checked and found to be exactly the same. Although we have not recycled the sample any further, one can expect that considering with hydrolytic stability of the sulphonamide linkages; the chelating polymer is reusable many times.

Table 2
Boron release from loaded sample (0.25 g) by action of 20 mL HCl solution (4 M)

Reaction time	Boric acid recovered (mmol g^{-1})	Percentage[a] releasing
30 min	3.20	97.6
60 min	3.22	98.2
120 min	3.23	98.5
24 h	3.22	98.2

[a] Based on boron loaded polymer.

Table 3
Effect of pH on the boron uptake

H_3BO_3 (M)	Buffer (pH)	Boron sorption[a] capacity (mmol g^{-1})
0.485	2.0	1.7
0.485	4.05	1.95
0.485	5.0	2.95
0.485	7.4 (non-buffered)	3.29
0.485	8.0	3.31

[a] By carminic acid method.

Table 4
Effect of foreign ions on the boron sorption

H_3BO_3 (M)	Foreign ions	Sorption of the foreign ion (mmol g^{-1})	Boron sorption (mmol g^{-1})
0.41	0.14 M, Mg (II)	0.15	3.25 ± 0.03
0.41	0.14 M, Ca (II)	0.14	3.20 ± 0.03
–	0.20 M, Mg (II)	0.16	–
–	0.20 M, Ca (II)	0.15	–
0.41	0.20 M, Fe (III)	0.43	3.15 ± 0.04

Effects of pH and some foreign ions do not differ from those of the spherical bead resins having similar boron chelating ligands on their surfaces [9]. The boron uptake markedly increases when pH > 5. While in acid region there is a competition between complexation and decomplexation of boric acid (Table 3).

To investigate possible interferences of foreign ions boron uptake experiments were performed in the presence of Ca(II), Mg(II) and Fe(III) ions. These ions were found to be also absorbed in minor quantities (Table 4). However, sorption of these ions is due to precipitation of their hydroxides onto the particles rather than donor–acceptor complex formation, as discussed before [8]. Fortunately presence of the foreign ions does not induce any significant change in the boron uptake capacity of the resin, presumably owing to partial adsorption of boric acid on the surfaces of metal hydroxides.

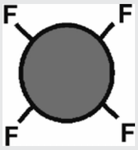
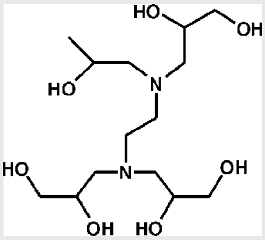
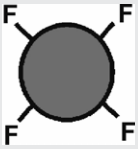
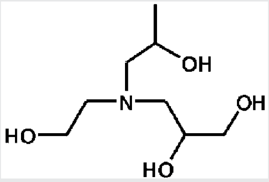
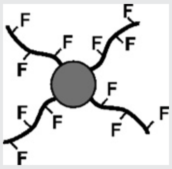
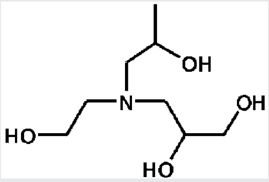
4. Conclusions

The new resin presented in this study appears to be superior to traditional bead polymers in chelating with boron in many respects, as shown in Table 5. Distinct advantages of this material can be summarized as follows:

- It is possible to remove trace boron in less than 2 min of contact, which is in fact an extremely short time as compared with those for conventional resins (30–35 min). This makes the present material superior to conventional chelating resins.
- Unlike conventional resins, capacity of boron uptake is nearly equal to the theoretical capacity. This implies that all the chelating units involve in boron uptake.
- Since (PS-DVB)-*graft*-PGMA is obtainable by surface initiated ATRP of GMA, chain lengths of the surface grafts are controllable, which makes density of the boron chelating units a tunable parameter. Thus, this strategy allows preparing boron chelating resins with desired sorption capacities.

For a wider scope for this work, oxirane groups of the base polymer offer many modification possibilities for preparing new functional polymers as catalysts or reagent carriers. In such a macromolecular topology, quasi-homogenous reaction conditions provided by flexibility of the functionalized graft chains are combined with easy isolation facilities of the crosslinked microspheres.

Table 5
Comparison of boron uptake efficiencies of the different resins with aminopropylene glycol functions

Structure of the base polymer	Chelating group (F)	Functional group density (mmol g^{-1})	Boron loading capacity (mmol g^{-1})	Boron uptake per chelating group	Contact time for removal of trace boron
		3.9	3.0	0.77	80 min (Ref. [8])
		1.82	1.6	0.879	30 min (Ref. [9])
		3.28	3.29 ± 0.02	1.0	<2 min (This study)

Acknowledgments

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