

Chemical modification of cellulose for boron sorption from water solutions

A. Sarsenov¹, V.K. Bishimbaev¹, B.A. Kapsalamov¹, K.K. Lepesov¹, K.M. Gapparova¹,
P. Grzesiak^{2*}

¹Social Fund “Research Centre of Salt Technology”, BC Ansar, 25 Syganak, 010000 Astana, Republic of Kazakhstan,

²Institute of Plant Protection – National Research Institute, Władysława Węgorka 20, 60-318 Poznań, Poland

*Corresponding author: e-mail: Grzesiak@iorpib.poznan.pl

It is shown that natural cellulose obtained from the walnut shell (*Juglans regia*) can be used for chemical modification of the selective boron sorbent. The modification was carried out by the coupling technique of chlorine derivatives of the polyhydric alcohols or polyols (mannitol, xylitol, sorbitol or glycerol). In this case new hybrid substances (sorbents) were obtained and they are represented by the formula: R-O-(CHOH)_n-CH₃, where R is a residue of the cellulose backbone, n is the number of functional (OH) groups of the polyhydric alcohols. The pulp mercerization was carried out by processing the ground walnut shell (WS) with hot solution of sodium hydroxide. Chlorination of polyhydric alcohols was carried out by gaseous hydrochloric acid sparging through the polyhydric alcohol aqueous solution. The coupling process proceeds according to the mechanism of substitution of the cellulose hydroxyl groups with chlorine atoms.

Keywords: cellulose chemistry, natural hybrid sorbents, modified cellulose.

INTRODUCTION

Boron is an important microelement necessary for normal plant life. Absence of boron stops their growth, causes various diseases in agricultural plants and is associated with disturbances in oxidative and energy processes in tissues, and leads to a decrease in the biosynthesis of basic substances. When there is a deficit of boron in the soil, microfertilizers such as boric acid, borax and others are used. This allows for increased yields and quality of products and helps eliminate some diseases of plants¹.

The influence of boron on a living organism is ambiguous. One of the rare types of corneal dystrophy is associated with a gene that encodes a transporter protein, presumably regulating intracellular boron concentration². On the other hand, exceeding its concentration adversely affects the environment and the human body. A number of works^{3, 4} are devoted to the role of boron in living organisms. Every day a person receives 1–3 mg of boron from food. The toxic dose is 4 g and the lethal dose (LD) is equal to about 6 g/kg of body weight. The results of the work presented in⁴ showed high levels of boron concentration in the lake water under investigation (vary from 8.64 to 16.73 mg/L). The highest level of boron in the lake was found in the liver of *Squalius cii* (34.64 mg/kg), followed by boron content in the body of *Limnodrilus hoffmeisteri* (2.84 mg/kg), *Chironomus tentans* (2.11 mg/kg) and *Gammarus pulex* 1.98 mg/kg⁴.

On the other hand, in connection with the depletion of raw materials, research on the extraction of boron from hydro-mineral raw materials is of current interest^{5–7}. Solving the issue of processing of hydro-mineral raw materials, many researchers show an interest in obtaining safe organic sorbents based on natural materials.

The literature describes the operating procedure of cellulose and polyatomic alcohols as components for the synthesis of various sorbents. For example, the studies^{8–10} describe production processes of composite sorbents using cellulosic fibrillated fibres together with iron and calcium compounds to extract inorganic ions

from aqueous solutions, but these works do not consider the extraction of boric acid.

“Method of Producing a Composite Sorbent Based on Carbonate and Magnesium Oxide” invention¹¹ proposes to obtain an effective sorbent for sewage treatment from metal ions by immobilizing finely dispersed MgCO₃ and Mg(OH)₂ onto fibrillated cellulose fibres containing more than 94% of fibers with the length less than 0.63 mm and more than 54% of fibres with a length less than 0.63 mm.

A patent of Russian Federation No. 2520457¹² is known in which a composite sorbent consisting of polyvinyl alcohol and nanophase oxyhydroxide extracted from wastes of groundwater deferrization stations is used to purify aqueous media from arsenic.

In the study¹³, carboxymethylcellulose (CMC) containing layered double hydroxides was synthesized by the ion exchange method. Experiments have shown that for such CMC the value of boron adsorption increases with increasing contact time, boron concentration and pH, up in the range of **3÷4 mg B per 1 gram of CMC**.

The study¹⁴ presents the research concerning boron removal from simulated and real water systems in the North of Chile using ultrafiltration enhanced by polymers in water. Poly-(glycidylmethacrylate-N-methyl-D-glucamine), (P (GMA-NMG)) was used to form complexes with boron, and the membrane with regenerated cellulose was used as a separator. The retention capacity of the polymer membrane was maintained at a level of 2–4 mg B per gram of polymer.

Two forms (powder and fibre) of N-methylglucamine cellulose derivatives were synthesized to produce adsorbents obtained from a natural polymer¹⁵. Adsorption capacities of cellulose derivatives for boron were the same as those of the commercially available N-methylglucamine type polystyrene resin. However, cellulose derivatives adsorbed boron (III) faster than polystyrene resin. It was found that the cellulose derivatives are superior to the polystyrene resin as boron (III) adsorbents for treating large amount of sewage.

In these studies, cellulose modification by mercerization followed by the introduction of industrial polyatomic alcohols into it was not also carried out.

It should be noted that a general disadvantage of sorbents obtained by using glucamine derivatives in the significant biodegradation of glucamine, as it is a nutrient source for bacteria^{15–17}.

There is no information in the literature^{8–24} on chemical modification of mercerized cellulose, by sewing chlorinated derivatives of polyhydric alcohols (matrix) to its polymeric carbon skeleton (matrix), and also on the structure and sorption properties of these compounds. Nevertheless, the interest of researchers in the study of cellulose derivatives as sorbents has been preserved to this day. Various types of cellulose, modified by mercerization methods (treatment with alkali solutions), and also by chemical modification of functional groups are of interest. Processed by such methods, cellulose acquires special selective properties, at the level of the best existing organic sorbents. It is attractive that a widely used natural material is applied. The research was carried out with the aim of searching for new functional materials with specified properties, as well as for justifying the choice of the directions of fundamental research.

The novelty of this study represents the first attempt to conduct a chemical grafting of chlorinated sorbitol (hexahydroxy sugar alcohol) into the matrix of cellulose in the form of walnut shell.

The goal of this study was to obtain selective sorbent from cellulose (the walnut shell) and to research redistribution of the initial boron content in the form of H_3BO_3 between phases of the aqueous solution and the sorbent, chemically modified cellulose.

To achieve these goals, the following tasks are set:

- chemical treatment of cellulose in order to improve its sorption properties;
- studying the sorbent structure;
- studying the sorption process mechanism and efficiency, both on modified and unmodified cellulose;
- identification of physicochemical regularities of interface distribution of boron in a solution-solid system.

MATERIAL AND METHODS

The ground walnut shell WS (*Juglans regia*) was chosen as raw materials suitable for its physicochemical and mechanical properties.

The boron concentration was determined by the spectrophotometric method of analysis under small amounts of boron and by acid-base titration in the presence of polyatomic alcohols of mannitol, xylitol, sorbitol at boron content of up to 1 g/L.

The composition of the substance was determined by independent methods of infra-red spectroscopy, elemental chemical and mass spectrometric analyses. Clarus SQ 8 gas chromatograph/mass spectrometer was used for the work.

Infra-red absorbance spectra of reaction products are registered on the IR-20B spectrophotometer in potassium bromide tablets in the range 600–3800 cm^{-1} .

Brief characteristics of techniques used in the research process are given below:

The method for boron determination

Quantitative determination of small boron concentrations was carried out with a photometric method with carmine presence, and for boron content of 10 mg/L

and more its determination was carried out by titration with mannitol^{25, 26}.

The sorption degree was determined as percentage ratio of the residual boron amount after extraction to its original content in the solution.

Determination of static exchange capacity

The sample mass of anion-exchange resin of 0.1–0.15 g (in OH⁻ form) is filled with 50 mL of 0.1 M HCl solutions and held for 24 hours at periodically mixing. The excess acid is determined by the titration with alkali in the presence of bromothymol blue indicator and it is calculated by a formula (1):

$$COE = \frac{(V_1 - V_2) \cdot M \cdot K \cdot f}{g} \quad (1)$$

where: V_1 is the amount of alkali, spent for titration in the control experiment, mL;

V_2 is the amount of alkali, spent for titration of the equilibrium solution, ml; M is alkali molarity; K is correction factor; f is sample mass of ion-exchange resin, g.

Study of the boric acid sorption by ion-exchange resins

The sample mass of ion-exchange resin of 0.10–0.15 g is filled with 50 mL of boric acid (of a certain concentration) in the relevant environment and held for 2 days until equilibrium is established under periodic shaking. Then the ion-exchange resin is filtered and the liquid phase is analysed for boron content. The H_3BO_3 sorption by ion-exchange resins under dynamic conditions was carried out by passing the boric acid solution of a certain concentration through the anion-exchange column by means of a measuring pump, followed by an analysis of a solution at column outlet.

A sample of natural cellulose was preliminarily ground, and then the fraction of 1.0–1.5 mm was screened out. The mercerization was carried out by treatment with sodium hydroxide 40% solution under the temperature of 80–90°C in the water bath for 2–3 hours.

After the modification process, the cellulose derivatives acquire the properties of ion-exchange resins with acceptable kinetic properties due to the fact that, in the swollen state, they have a high sorption rate due to the availability of its ionogenic groups. The synthesized sorbents have such advantages as cheapness, availability, the possibility of recycling (regeneration), non-toxicity, significant exchange capacity.

Under the mercerization, heteropolysaccharides of the walnut shell pass into the alkali solution³. In this treatment, the polymeric cellulose backbone is uncovered and the (OH) groups in it become more accessible. At that, the number of available nanopores with a diameter of up to 50–100 nm and micropores with a diameter greater than 100 nm are evidently increased.

The mercerized cellulose (MC) obtained from the walnut shell was washed with water up to neutral medium and dried at 105°C.

It was preliminary established that in a neutral medium the static exchange capacity for the walnut shell in pure H_3BO_3 solutions in distilled water (initial content of 5 mg/L of boron) is 0.030 mg of boron in 1g of sorbent. The exchange capacity in tap water is 0.080 mg of boron in 1g of sorbent (with the same boron content). It

is 0.120 mg of boron in 1g in tap water with xylitol (in a molar ratio of 1: 2).

The water used met the requirements of state standard 2874-82 "Potable Water"; boric acid was added in it the calculation of 5 mg/L of boron content.

Xylitol is chosen because this pentahydroxy sugar alcohol, like other polyatomic alcohols, forms complex compounds with boric acid, to the functional groups of the mercerized cellulose¹⁰.

For further work, taking this information into account, the walnut shell was selected for its further chemical treatment to introduce polyatomic alcohol derivatives into the polymer matrix of the walnut shell. This area of work was compared with the literature data.

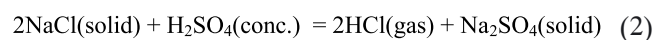
RESULTS AND DISCUSSIONS

As can be seen from the above, the species of the walnut shell obtained by us have no appreciable selectivity to boron, and the addition of polyatomic alcohol increases its sorption capacity by 1.5 times to 100 mg of boron in 1g of sorbent. However, the addition of alcohol directly to the aqueous solution is not expedient because it additionally pollutes water with organic matters. Therefore, it was decided to introduce polyol residues of alcohol into the skeleton of modified cellulose (MC).

To improve capacity of the modified cellulose sorbent, it was additionally modified by chemically coupled molecules of hexahydroxy alcohol (sorbitol). The suggested method was used for the first time to conduct the synthesis in two stages.

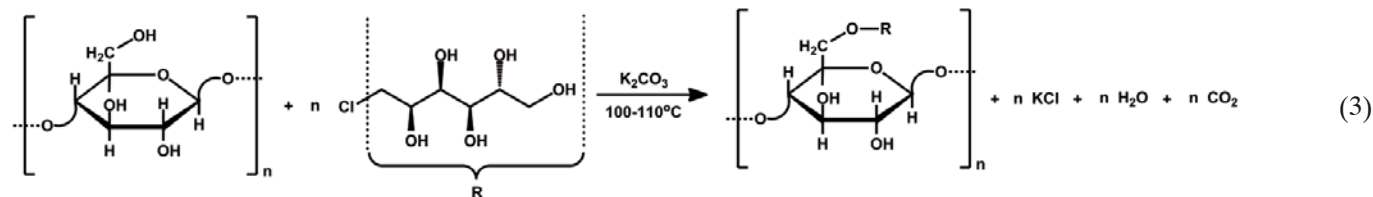
I stage – synthesis of 1-chloro- and 1,6-dichlorosorbitol. The chlorinating agent (hydrochloric acid) was prepared by a known reaction when the mixture heating to 70°C: $2\text{NaCl}(\text{solid}) + \text{H}_2\text{SO}_4(\text{conc.}) = 2\text{HCl}(\text{gas}) + \text{Na}_2\text{SO}_4(\text{solid})$

Hexahydroxy alcohol – sorbitol is treated with hydrogen chloride at 95 °C in toluene for 6 hours.



The reaction product is treated with a solution of sodium carbonate up to neutral media, and then washed several times with water. After separation of the aqueous layer, the mixture of the chlorine derivatives of sorbitol is purified by distillation in the range of 85–100°C.

II stage – chlorinated sorbitol is coupled chemically to mercerized cellulose at 100–110°C in the presence of 10% K_2CO_3 solution for 5 hours:



where R is the residue of polyatomic alcohol coupled to the cellulose monomer.

The reaction product is filtered, washed with water, alcohol and again with water up to neutral media, then it is brought to an air-dried state.

Infra-red spectra in the 3400–3200 cm^{-1} range has an intensive wide band of stretching vibrations ν that arise

when intermolecular hydrogen bonds (poly-associates) are formed. For the MC the bands in the 1400–1000 cm^{-1} range (νOH) appear more intensively because the number of (OH) groups in MC was increased. Here we also observe a very weak absorption band in the range 700 cm^{-1} characteristic for the chlorine atom (νCl), which indicates a practically complete absence of chlorine in MC.

In the spectra of chlorinated sorbitol, vice versa, we can judge about the substitution of two primary (OH) groups for chlorine atoms by significant increase of the intensity of the vibration bands involving (C-Cl) bond.

In the range of 2930 cm^{-1} and 2865 cm^{-1} there are strong bands characterizing the asymmetric and symmetric valence vibrations of the methylene group (CH_2), and there is also a deformation vibration band (C-H) in the 1450 cm^{-1} range.

In addition, in the spectrum, variable absorption bands are observed in the 1375–1300 cm^{-1} range associated with the deformation vibration of the (OH) group, and in the 1080–1030 cm^{-1} range associated with the vibration, in the formation of which the bond stretching (C-O) takes part.

Coupling of chlorinated sorbitol proceeds quite fully and this is proved by minimizing the band of stretching vibrations νCl in the range of 700 cm^{-1} .

In the range of 970–900 cm^{-1} the average nonplanar absorption bands characteristic for deformation vibrations of methane groups (CH) are observed.

In the range of 750–700 cm^{-1} , intense narrow vibration bands characteristic for the (C-Cl) bond as in the mixture of the chlorinated derivatives of sorbitol and in the finished product appear. This means that not only 1-chloro- but 1,6 dichlorosorbitol is coupling. Calculation according to the ratio of C/H in the monomer showed that the coupling of mono- and dichloro-derivatives is likely to be equally probable, since for both chlorine derivatives the C/H ratio is practically identical with the ratio 1:1.43 given above, which was calculated from the data of elemental chemical analysis.

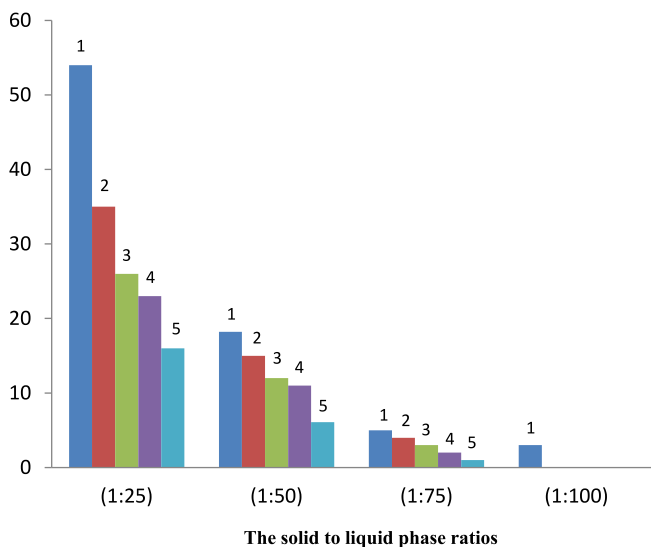
In equilibrium and dynamic conditions, the dependencies of boron extraction from aqueous solutions on unmodified (UMC) and modified (MC) cellulose at various initial concentrations of boron, contact time and phase ratios (solid to liquid) were studied. Dependencies are given in comparison with each other; they are investigated in comparison with unmodified cellulose. The experimental data obtained are shown in Fig. 1 for the UMC and in Fig. 2 for MC, and also in Table.1, in

which the experimental data were processed with the help a linear dependence $Y = aX + b$, where Y is the boron extraction degree, (% – percentage of the boron initial concentration); X is the initial boron concentration in the solution (g/L); a , b are empirical coefficients.

These dependencies were determined to identify the dynamics of the change in the degree of boron extraction

Table 1. The dynamics of the change in boron extraction degree on solid to liquid phase ratio for different boron initial concentrations when using UMC

No./No.	Boron initial concentration, g/L	$y = ax + b$	Coefficient of approximation R^2 (correlation)
1	0.023	$y = -16.62x + 61.6$	0.8254
2	0.039	$y = -11.6x + 42.5$	0.9129
3	0.048	$y = -8.7x + 32$	0.9259
4	0.073	$y = -7.8x + 28.5$	0.9218
5	0.089	$y = -5.31x + 19.05$	0.8767

**Figure 1.** Dependence of the change of boron extraction degree on solid to liquid phase ratios. Sorbent -unmodified cellulose. Initial boron concentration in the solution, g/L: 1–0.023 g/L; 2–0.039 g/L; 3–0.048 g/L; 4–0.073 g/L; 5–0.089 g/L

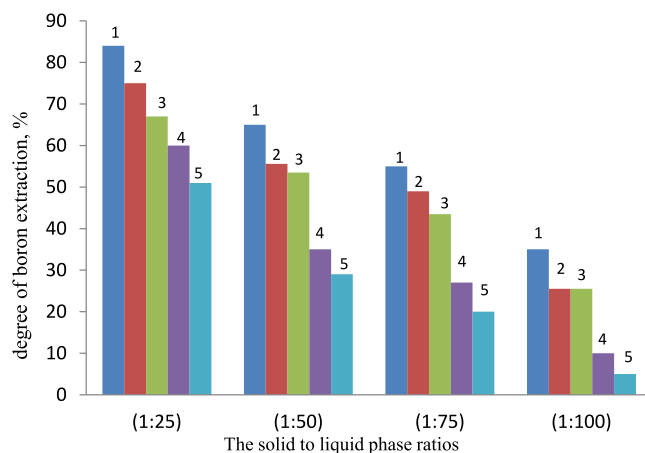
on solid to liquid phase ratio for different boron initial concentrations when using UMC.

It can be seen in Fig. 1 that the boron extraction degree decreases when increasing the mass ratio of solid and liquid phases, i.e. the ratio of the sorbent mass to the solution mass; this is due to a relative increase in the total amount of boron compared to the same amount of sorbent.

When decreasing the initial boron concentration from practically 0.09 to 0.02 g/L in the solution, the degree of its extraction by the unmodified cellulose (UMC) sorbent increases up to 55%, i.e. by almost 11% for every 0.02 g of boron concentration decrease.

Fig. 2 shows also the dependence for modified cellulose (MC). It should be noted that both types of cellulose tested were mercerized (treated with alkali solution), but chemical coupling of polyatomic alcohol was carried out only for the modification of cellulose (MC).

It can be seen in Fig. 2 that modified cellulose (MC) is much more efficient sorbent at the same boron concentrations and the same solid:liquid phase ratios. All other things being equal, the boron extraction degree increases two times faster at the modified cellulose (MC) than at unmodified cellulose (UMC). The degree of

**Figure 2.** The dependence of the change of boron extraction degree on solid to liquid phase ratios. Sorbent-modified cellulose. Initial boron concentration in the solution, g/L: 1–0.023; 2–0.039; 3–0.048; 4–0.073; 5–0.089

sorption increase is more significant for average values of concentrations, as well as for average values of the ratio of sorbent and solution masses.

On one hand, this is due to an increase of saturation degree and diffusion difficulties in the sorbent phase as the equilibrium is approached, and on the other hand, this is due to decrease of saturation degree when increasing solid:liquid phase ratios, i.e. two parameters of the sorption process affect the magnitude of the increase in different directions, that is why for average values of parameters the sorption process proceeds more efficiently.

Table 2 shows the equations of the dependence of boron extraction degree on solid:liquid phase ratio.

Based on the calculations, a combined empirical equation is obtained that relates the dependence of the influence of initial boron concentration and solid to liquid phase ratio on the extraction value. This equation for unmodified cellulose (UMC) is expressed by the formula: $Y = (102.93 - 1.3538 \cdot Z) - (1025.4 - 13.937 \cdot Z) \cdot X$ (4) where: Y is the percentage of boron sorption; X is the initial concentration in solution, g/L; Z is solid to liquid phase ratio.

Graphically this dependence is shown in the form of a diagram in Fig. 2. Similarly, the dependence of the change of boron extraction degree on its initial con-

Table 2. The dynamics of the change of boron extraction degree on solid to liquid phase ratio for different boron initial concentrations when using MC

No./No.	Boron initial concentration, g/L	$y = ax + b$	Coefficient of approximation R^2 (correlation)
1	0.023	$y = -15.7x + 99$	0.9854
2	0.039	$y = -15.5x + 90.05$	0.96140
3	0.048	$y = -13.45x + 81$	0.9873
4	0.073	$y = -15.8x + 72.5$	0.9616
5	0.089	$y = -14.7x + 63$	0.9727

centration at different solid to liquid phase ratios was found. Sorbent – modified cellulose.

$$Y = (116.55 - 0.6691 \cdot (Z) - 632.14 - 1.3214 \cdot Z +) \cdot X \quad (5)$$

Comparison of formulas 4 and 5 shows that under identical sorption conditions, the modified cellulose (MC) is much more efficient than the unmodified cellulose (UMC). For example, with an initial boron concentration of 0.02 g/L and with the liquid to solid phase ratios of 55:1, the extraction degree of 50% of the initial value is obtained at the unmodified cellulose; and with the use of MC (modified cellulose), the extraction degree reaches almost 80%. Consequently, the modified cellulose is 1.6 times better extracted by H₃BO₃ than the unmodified cellulose in comparable conditions. Regeneration of the modified cellulose is possible with 3% HCl or H₂SO₄ to obtain solutions with boron content up to 10 g/L²⁸.

It should be noted that the modified cellulose can be used as an enter sorbent for acute and chronic intoxication of people at manufacturing site and in the boron biogeochemical provinces. In this connection, it is expedient to use the proposed sorbent to remove boron excess out of therapeutic, mud-salt cosmetic compositions based on the brine of the saline lakes in the Aral Sea region, and also to reduce the boron concentration below the maximum permissible concentration (0.5 mg/L) in the boron biogeochemical provinces of Western Kazakhstan.

It is of interest to introduce a powder of ground sorbent into water-soluble medical and cosmetic compositions based on boron-containing hydro-mineral raw materials. This will help to neutralize the harmful effect of boron compounds excess on the human body, as well as to improve the quality of marketable products of the cosmetic and pharmaceutical industries derived from brine and silt of saline lakes, sea water, technogenic sewage and still waste liquid of soda production.

CONCLUSION

The study of the interphase distribution of boric acid between aqueous solutions and the solid phase of chemically modified cellulose, the results of which are given in this paper, creates the scientific base for the technology of processing and utilization of natural and industry-related boron-containing hydro-mineral raw materials.

As the produced sorbent is not toxic, it has the following advantages:

- a potential application of the sorbent for the purification of the therapeutic mud from boron;
- use of the sorbent for obtaining boric microfertilizers;
- the sorbent can be obtained by recycling the wastes of agricultural industry;
- above mentioned formulas (5, 6) allow for the extrapolation of the dependencies of boron extraction without conducting additional experimental procedures;
- the developed sorbent is produced from natural materials, which are environmentally safe and relatively inexpensive substances to obtain.

Based on the conducted studies, the following conclusions should be made:

- A new method for obtaining an efficient boron-selective MC sorbent was developed by chemical coupling to mercerized natural cellulose of chlorinated derivatives of polyatomic alcohols;

– Modified cellulose, being a more accessible and cheap sorbent, under otherwise equal conditions, is highly competitive with the best boron-selective ion exchange resins of the BA type (Boronium anionite).

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