Chemical Modification of Cellulose by Chlorinated Derivatives of Polyatomic Alcohols for Obtaining Selective Sorbent

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Abstract

It is shown that natural cellulose in the form of a walnut shell (Juglans regia) is reasonable to use for chemical modification for the purpose of manufacturing a boron-selective sorbent. The modification is carried out by the coupling technique of chlorinated derivatives of the polyatomic alcohols (mannitol, xylitol, sorbitol or glycyl alcohol). In this case new hybrid substances (sorbents) are obtained and they are represented by formula: R-O (CHOH)n-CH$_3$, where R is the residue of the cellulose backbone, n is the number of functional (OH) groups of the polyatomic alcohol. The pulp pre-mercerizing was carried out by processing the ground walnut shell (WS) with solutions of sodium hydroxide upon the application of heat. Chlorination of polyatomic alcohols was carried out by the gaseous hydrochloric acid sparging through the aqueous solution of polyatomic alcohol. The reaction proceeds by the mechanism of nucleophilic substitution. The coupling process proceeds according to the mechanism of substitution of the cellulose hydroxyl groups with chlorine atoms, forming part of monochloro-derivatives and dichloro-derivatives of polyatomic alcohol.

Based on the elemental, chemical and mass-spectrometric analysis carried out, and on the study of the infra-red spectrum of the new hybrid substance, its structure is given, and the chemisorbtion mechanism of boric acid by hydroxylated residues of the modified natural cellulose backbone.

Visualization techniques of data on the boron sorption analytically (by formulae) and graphically (by diagram) are proposed.

It is suggested to use MC as an enterosorbent for chronic and acute intoxication of people with toxic boron compounds.

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

INTRODUCTION

As a raw material, the ground walnut shell WS (Juglans regia) was chosen as 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 a boron content of up to 1 g/l (relative error of the analysis was ± 4.0%) etc. [1, 2, 3]. Below are brief characteristics of the techniques that were used in the research process:

The method for boron determination

Quantitative determination of low boron concentrations was carried out with a photometric method with carmine, and with a boron content of 10 mg/l and more its determination was carried out by titration with mannitol [4, 5].

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

Determination of static exchange capacity

The sample weight of ion exchanger of 0.1 - 0.15 g (in OH$^-$ form) is filled with 50 ml of 0.1 N HCl solutions and allowed for 24 hours, periodically mixing. The excess acid is determined by titration with alkali in the presence of the bromothymol blue indicator.

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

where: V$_1$ - the amount of alkali, used for titration in the blank determination, ml;

V$_2$ - the amount of alkali, used for titration of the equilibrium solution, ml;

N – alkali normality;

K – current factor;

f – The sample weight of ion exchanger in g.

Study of the boric acid sorption by ion exchangers

The sample weight of ion exchanger of 0.0001±0.0002 g is filled with 50 ml of boric acid (of the certain concentration) in the applicable environment and allowed for 2.0 days until equilibrium is established under intermittent shaking. Then the ion exchanger is filtered, and the liquid phase is analysed for boron. The sorption of H$_3$BO$_3$ by ion exchangers under dynamic conditions was carried out by passing the boric acid solution of the certain concentration through the ion exchanger column by means of a measuring pump, followed by solution analysis as it leave the column.

The kinetics of boron sorption was studied by the limited volume method, which is outlined as follows: 50 ml of the H$_3$BO$_3$ solution (about 0.030 mg V/l) is introduced into the temperature-controlled cell, after the thermodynamic equilibrium is established, 0.20 g of sorbent is added in the form of free amine at the solid to liquid ratio: – 1: 250. At specific time intervals the ion exchanger is separated and an aliquot of the solution (25 ml) is filtered off for boron content. After the modification process, the cellulose derivatives acquire the properties of ion exchangers 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 repeated use (regeneration), non-toxicity, significant exchange capacity.

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 a 40% solution of sodium hydroxide under the temperature of 80-90 °C in the water bath for 2 - 3 hours.

Under the mercerization, heteropolysaccharides of the walnut shell pass into the alkali solution [3]. In this treatment, the polymeric cellulose backbone is revealed and the (OH) groups in it become more accessible. In this case, the number of available nanopores with a diameter of up to 50-100 nm and micropores with a diameter greater than 100 nm is evidently increasing.

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

It was preliminary established that in a neutral environment the static exchange capacity for the walnut shell using pure H$_3$BO$_3$ solutions in distilled water (initial content of 5 mg/l B) is 0.030 mg V/g sorbent, using tap water it is 0.080 mg V/g (with the same boron content). Using tap water with xylitol (in a molar ratio of 1: 2) it is 0.120 mg V/g.

The water used was in accordance with GOST 2874-82 Drinking Water, in which boric acid was added in the calculation of 5 mg/l in boron content.

Xylitol is chosen because this pentatomic alcohol, like other polyatomic alcohols, forms complex compounds with boric acid, to the functional groups of the mercerized cellulose [3].

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

The literature describes the operating procedure of cellulose and polyatomic alcohols as components for the synthesis of various sorbents. For example, the studies [6, 7, 8] describes 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.

In the A Method for Producing A Composite Sorbent Based on Carbonate And Magnesium Oxide invention [9], it is proposed to obtain an effective sorbent for wastewater treatment from metal ions by immobilizing finely dispersed $MgCO_3$ and $Mg(OH)_2$ onto fibrillated cellulose fibres containing not less than 94% of fibers with the length not more than 0.63 mm and not less than 54% of fibres with a length not more than 0.63 mm.

In the patent of the Russian Federation No. 2528696 [10] it is proposed to obtain a sorbent by treating fibrillated cellulose fibres in the solution of a zinc salt of hydroxides and/or with sodium sulphide to recovery silver and phosphorus.

A patent of the Russian Federation No. 2520457 [11] is known as such in which a composite sorbent consisting of polyvinyl alcohol and nanophase oxyhydroxide isolated from wastes of groundwater deferrization stations is used to purify aqueous media from arsenic.

In the study [12], carboxylmethylcellulose (CMC) containing layered double hydroxides was synthesized by the ion exchange method [12]. Experiments have shown that for such CMC the value of boron adsorption increases with increasing contact time, boron concentration and pH, up to 3÷4 mg B per 1 gram of CMC.

The study [13] presents the research of 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 the 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 polymer [14]. The adsorption capacities of the boron cellulose derivatives 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 a large amount of waste water.

In these studies, too, no modification of cellulose by mercerization followed by the introduction of industrial polyatomic alcohols into it was also carried out.

It should be noted that the general lack of sorbents obtained by using glucamine derivatives consists in a significant biodegradation of glucamine, because the latter is a nutrient substance for bacteria [6-24].

Thus, there is no information in the literature on the chemical modification of mercerized cellulose by coupling chlorinated derivatives of polyatomic alcohols to its polymeric carbon skeleton (matrix), as well as no information 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 up to the present moment.

The goal of this study was to research the redistribution of the initial boron content in the form of H_3BO_3 between the phases of the aqueous solution and the sorbent through time, on chemically modified cellulose.

To achieve this goal, the following tasks are set:
– chemical treatment of cellulose in order to improve its sorption properties;
– structural determination of sorbent; and
– establishment of a mechanism for the efficiency of the sorption process on modified and unmodified cellulose of the walnut shell;
– identification of physicochemical regularities of interphase distribution of boron in a solution-solid system.

EXPERIMENTALS

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 1.5-4.0 times to 100 mg of V/g sorbent. However, the addition of alcohol directly to the aqueous solution is not advisable because it additionally pollutes the water with organic matters. Therefore, it was decided to introduce polyol residues of alcohol into the skeleton of modified cellulose (MC).

To improve the capacity of the modified cellulose sorbent, it was additionally modified by chemically coupled molecules of hexatomic alcohol (sorbitol). The synthesis was carried out in two stages.

I stage - synthesis of 1-chloro- and 1,6-dichlorosorbite. The chlorinating agent (hydrochloric acid) was prepared by a known reaction when the mixture was heated to 70°C:

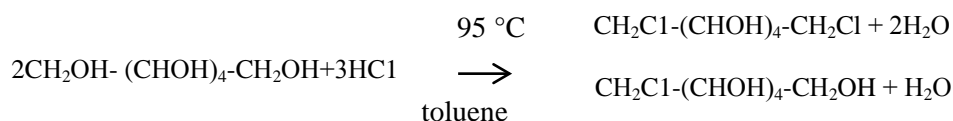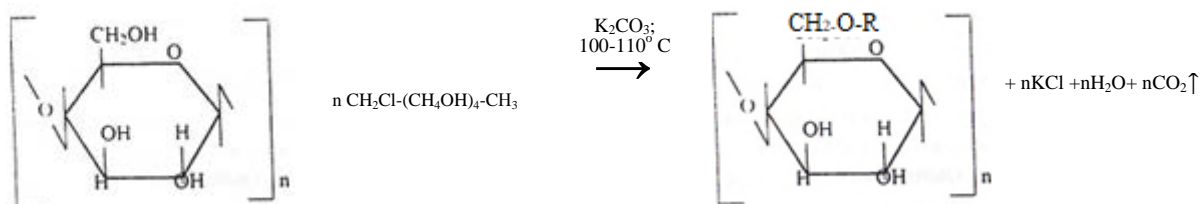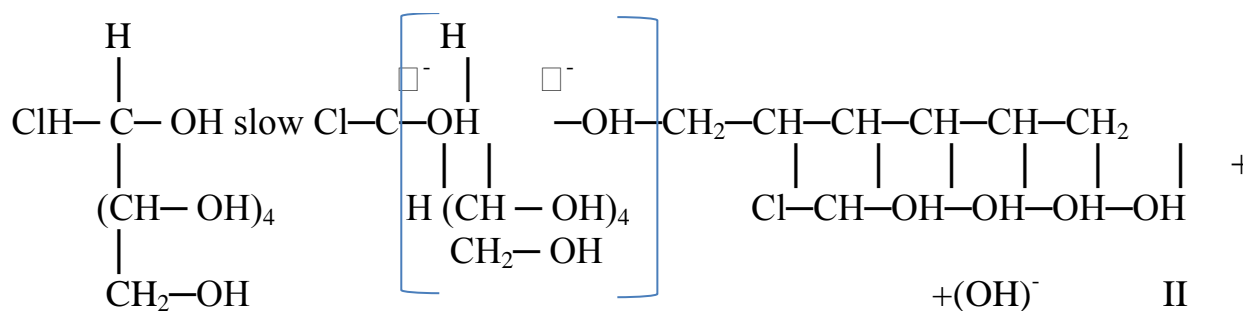$$2NaCl(solid) + H_2SO_4(conc.) = 2HCl(gas) + Na_2SO_4(solid)$$
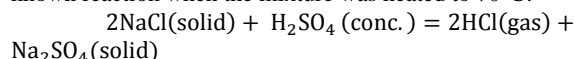
Hexatomic alcohol - sorbitol is treated with hydrogen chloride at 95 °C in toluene for 6 hours.

The reaction product is treated with a solution of sodium carbonate until neutral, and then washed several times with water. After separation of the aqueous layer, the mixture of the chlorinated derivatives of sorbitol is purified by distillation in the range of 85-100%.

There are two alcohol groups in the molecule, and moreover the primary groups are more active in the substitution reactions. Probably, the reaction proceeds according to the SN_2 mechanism (biomolecular nucleophilic substitution)

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

$$2CH_2OH\text{-}(CHOH)_4\text{-}CH_2OH + 3HCl \xrightarrow[\text{toluene}]{95\ °C}$$

$$CH_2Cl\text{-}(CHOH)_4\text{-}CH_2Cl + 2H_2O$$

$$CH_2Cl\text{-}(CHOH)_4\text{-}CH_2OH + H_2O \qquad I$$

II

$$K_2CO_3; \quad 100\text{-}110^\circ C$$

$$n\ CH_2Cl\text{-}(CH_4OH)_4\text{-}CH_3 \quad \longrightarrow \quad + nKCl + nH_2O + nCO_2\uparrow$$

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

III

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

No./No.	the initial concentration of boron, g/l	y= ax+b	the 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

The reaction product is filtered off, washed with water, alcohol and again with water until neutral, then it is brought to an air-dried basis. 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 work.

The 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}.

The percentage of carbon and hydrogen were equal: C-78.85%, H-9.65%. The ratio of carbon and hydrogen atoms calculated from these data is 1:1.41 and practically coincides with their theoretical ratio in monomer.

The calculation was made using the well-known method for determining the formula of a chemical compound based on its percentage and element composition:

C:H=78.85/12.0: 9.65/1.0 = 6.57:9.65 = 1:1.45

In the infra-red spectra in the 3400-3200 cm^{-1} range, there is an intense wide band of stretching vibrations ὐ that arise when intermolecular hydrogen bonds (poly-associates) are formed. For the MC the bands in the 1400-1000 cm^{-1} range (ὐ$_{OH}$) appear more intensively because the number of (OH) groups in the MC is increased. Here we also observe a very weak absorption band in the range of 700 cm^{-1} characteristic for the chlorine atom (ὐ$_{Cl}$), which indicates a practically complete absence of chlorine in the MC.

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

In the range of 2930 cm^{-1} and 2865 cm^{-1} there are strong bands characterizing the antisymmetric 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 ὐ$_{Cl}$ 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. The latter means that not only 1-chloro- but 1,6 dichlorosorbite 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.

RESULTS AND DISCUSSION

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 of Excel as a linear dependency Y = aX + b, where Y is the boron recovery rate, (%); 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 from the solid to liquid phase ratio for different initial concentrations of boron when using UMC.

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

With a decrease in 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.
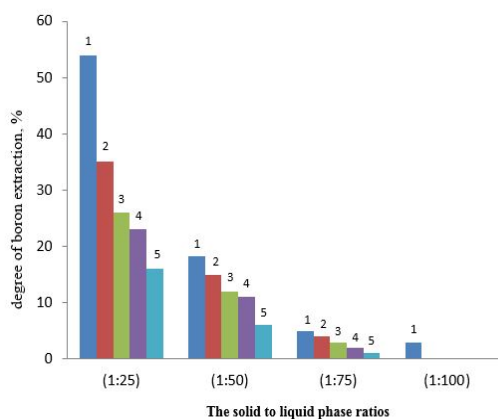
The initial boron concentration in the solution, g/l:
1-0.023 g/l; 2-0.039 g/l; 3-0.048 g/l; 4-0.073 g/l; 5- 0.089 g/l.
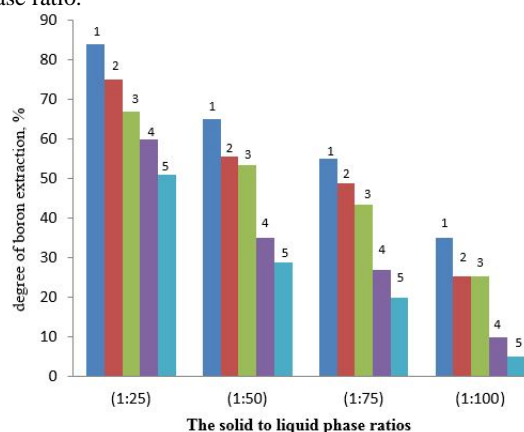
Figure 1. The dependency of the change of boron extraction on the solid to liquid phase ratios. Sorbent -unmodified cellulose.

Fig. 2 shows also the dependency 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. 1 that modified cellulose (MC) is a much more efficient sorbent at the same boron concentrations and the same solid and liquid phase ratios. All other things being equal, the degree of boron extraction is two times faster at the modified cellulose (MC) than at unmodified cellulose (UMC). The degree of increase in sorption is more significant for average values of concentrations, as well as the average values of the ratio of sorbent and solution masses.

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

proceeds more efficiently. Table 2 shows the equations of the dependency of the boron extraction degree on the solid and liquid phase ratio.

The initial boron concentration in the solution, g/l:
1-0.023; 2-0.039; 3-0.048; 4-0.073; 5-0.089

Figure 2. The dependency of the change of boron extraction on the solid to liquid phase ratios. Sorbent -modified cellulose.

Based on the calculations by the Microsoft Excel program, a combined empirical equation is obtained that relates the dependency of the influence of the initial boron concentration and the 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 · Z) - (1025.4 -13.937 · Z) · X (1)

where: Y is the percentage of boron sorption; X is the initial concentration in solution, g/l; Z is the solid to liquid phase ratio.

Graphically this dependency is shown in the form of a diagram in the following figure 3.

Similarly, the dependency of the change in the degree of boron extraction on its initial concentration at different solid to liquid phase ratios was found. Sorbent - modified cellulose.

Y = (116.55-0.6691 · (Z)-632.14 -1.3214 · Z +) · X (2)

When constructing the graphs in Fig. 3 and Fig. 4, the values of the solid to liquid phase ratios were replaced by the inverse liquid to solid phase ratios. Such a replacement was carried out to determine the dependency of the change in the degree of boron extraction on its initial concentration at different solid to liquid phase ratios (L:S) was found. Comparison of Figures 3 and 4 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 reaches almost 80%. Consequently, in comparable conditions the modified cellulose is 1.6 times better extracted by H_3BO_3 than the unmodified cellulose. Regeneration of the modified cellulose is possible with 3% HCl or H_2SO_4 to obtain solutions with boron content up to 10 g/l [3].

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

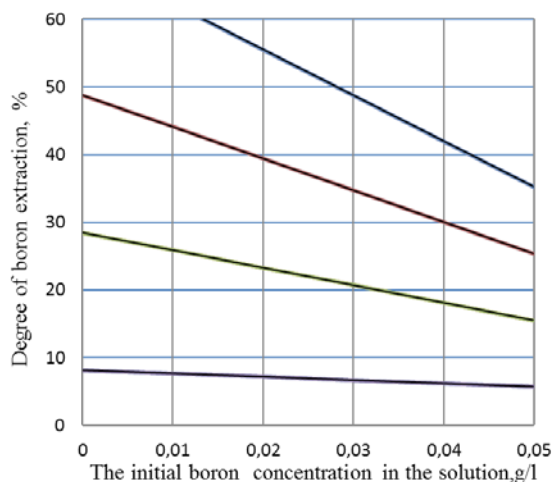| No./No.	the initial concentration of boron, g/l	y= ax+b	the coefficient of approximation R^2 (correlation)
1	0.023	y = -15.7x + 99	0.9854
2	0.039	y = -15.5x + 90.05	0.96140
3	0.048	y = -13.45x + 81	0.9873
4	0.073	y = -15.8x + 72.5	0.9616
5	0.089	y = -14.7x + 63	0.9727

Figure 3. The dependency of the change in the degree of boron extraction on its initial concentration at different solid to liquid phase ratios. Sorbent - unmodified cellulose.
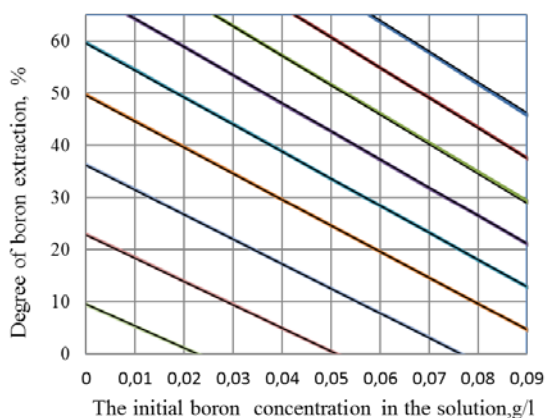

Figure 4. The dependency of the change in the degree of boron extraction on its initial concentration at different solid to liquid phase ratios.
Sorbent - modified cellulose.

It should be noted that the modified cellulose can be used as an enterosorbent for acute and chronic intoxication of people at manufacturing site and in the boron biogeochemical provinces. In this connection, it is advisable 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 improve the quality of marketable products of the cosmetic and pharmaceutical industries derived from brine and silt of saline lakes, sea water, industry-related waste water 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 basis for the technology of processing and utilization of natural and industry-related boron-containing hydro-mineral raw materials.

In the literature [12-19], there is the information that the processing of the obtained boron-concentrated water for micronutrients is economically feasible and environmentally justified. On the basis of the conducted studies, the following conclusions should be drawn:

- 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, with all other things being equal, is not inferior to the best boron-selective ion exchangers of the BA type (Boronium anionite) by its sorption characteristics.

Experimental data on the study of the interphase distribution of substance in heterogeneous systems (L-S) is proposed to be depicted in the analytical and graphical form (diagram), taking into account three variables (ratio of phase mass, concentration and extraction percent). The visualization of data in the form of such diagrams makes it possible to evaluate the efficiency of sorption for specified process parameters without setting up additional experiments.

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