New boron selective sorbents for sorption – membrane hybrid system

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Abstract: The synthesis and properties of core-shell sorbents dedicated to the removal of borates from aqueous solutions were described. By modification of polymer matrices with vinylbenzyl chloride followed by its derivatization with N-methyl glucamine a new kind of sorbents were obtained. The testing of boron sorption reviled that the process efficiency was related to the pore diameter and the content of ligand in the sorbent. The best material for use in a hybrid system, where boron is absorbed by fine particles and removed in microfiltration, was Poropak Q with a specific surface area of 300 m^2/g.

Keywords: borates, aqueous solutions, core-shell sorbents.

Nowe selektywne sorbenty borowe do hybrydowego systemu sorpcja – membrana

Streszczenie: Opisano syntezę i właściwości sorbentów typu rdzeń-otoczka przeznaczonych do usuwania boranów z roztworów wodnych. Poprzez modyfikację matryc polimerowych chlorkiem winylobenzylu, a następnie ich derywatyzację za pomocą N-metyloglukaminy otrzymano nowy rodzaj sorbentów. Badania sorpcji boru wykazały zależność wydajności procesu od średnicy porów i zawartości ligandu w sorbencie. Najlepszym materiałem do zastosowania w systemie hybrydowym, w którym bor jest absorbowany przez drobne cząstki i usuwany w procesie mikrofiltracji, okazał się Poropak Q o powierzchni właściwej 300 m^2/g.

Słowa kluczowe: borany, roztwory wodne, sorbenty typu rdzeń-otoczka.

The membrane separations have become important industrial applications since the 80-ties of the XX century. Among them, the pressure-driven process took the leading position. Depending on the size of separated compounds it is needed to apply pressure that varies from 0.2 bar for microfiltration to 80 bar for reverse osmosis. It should be noted here, however, that boosting pressure increases separation cost significantly [1]. For that reason, a search for new method of small molecules cheap separation is still open. One of the investigated options is the hybrid method that merges selective sorption on larger sorbent particles followed by the separation of obtained complexes by micro or ultrafiltration. There are two benefits of the sorption-based hybrid process use: high separation efficiency and low operational cost [1].

Now, in a time of water shortage, we have to use either brackish or wastewater. Both of them have to be treated first to remove some harmful compounds and elements. According to the guideline of WHO, the permissible level of boron for potable water is 2.4 mg/L and is kept below 1 mg/L for irrigation water. Removal of boron from aqueous solution was investigated in last decades and reported in many papers [2–11]. The idea for the use of the hybrid system, with fine solid particles caring N methyl-D-glutamine ligands, was tested successfully for deboronation of geothermal and seawater [2-5]. However, suitable fine sorbent particles were not available on the market. Hence, such particles were synthesized separately and used for the removal of boron [12, 13].

The studies of boron removal by selective sorbents revealed that the process was governed by pseudo-second-order kinetics and its efficiency was related to the size of the used particles [11]. These observations inspired us to synthesize core-shell sorbents and test them for the removal of borate [14, 15]. The obtained data showed that the core-shell structure was more efficient in separation than commercially available sorbents. However, these studies were carried out on one type of particle, with an average size of 600 micrometers and a surface of 750 m^2/g [14]. It was the starting point for the next series of tests when smaller particles were used. Preparation of the core-shell sorbents has been described in the literature, however, most of the reports used inorganic core particles to which some polymers were attached and functionalized [16, 17].

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To synthesize core-shell sorbent the following method was applied [14]. Polymer particles were impregnated with a mixture of monomer, crosslinker, solvent, and initiator. Then the monomers were thermally polymerized within the pores of core particles. The obtained materials were functionalized by N-methyl-D-glucamine to produce boron selective sorbents. To obtain fine particles, the Porapak™ porous polymer adsorbent (100 mesh) carriers were used. They were characterized by surfaces of 150, 300, and 550 m^2/g. The goal of the conducted studies was to develop the method for the preparation of fine sorbents for running the hybrid systems.

EXPERIMENTAL PART

Materials

Porapak™ porous polymer adsorbent samples with a surface area of 150, 300, and 350 m^2/g and particle diameter of 120-140 micrometers were purchased from Aldrich. Sorbent of XAD4 with particles size of 600 micrometers and 750 m^2/g surfaces was delivered by Aldrich. Monomers, vinyl benzyl chloride (VBC), and divinylbenzene (DVB) were used without any additional purification. Solvents, initiators, and other chemicals were also purchased from Aldrich.

Sorbents preparation

Sorbents were synthesized according to the method described previously [14]. Dry particles were impregnated overnight in the solution of VBC and DVB (9:1) in a 10:1 mixture of toluene and dodecyl alcohol (35 vol.% in respect to monomers). The impregnation mixture contained azobisbutylonitrile (0.2 wt.% to monomers). The swollen particles were centrifuged and suspended in a water phase containing poly(vinyl alcohol). Monomers in swollen polymer particles were polymerized at 90°C for 21 hours. The modified particles were filtered, rinsed with water, and dried. The modification with N-methylglucamine, NMGA, was carried out as follows: dry sorbents were swollen in 1,4-dioxane overnight, they were refluxed for 5 h with N-methyl glucamine solution (5:1 N:Cl molar ratio), filtered and extensively washed with acetone, cold and hot water. The samples were used in swollen form for further tests.

Methods

The amounts of the chloromethyl groups and nitrogen groups in the samples were estimated by Schoninger's [18] and Kjedahl's [19] methods.

Modification degree was calculated gravimetrically: increase of sample weight was normalized to the total weight of the modified sample.

The porous structure of the materials was evaluated using an Autosorb IQ analyzer by N_2 adsorption at 77 K. The specific surface area (S_{BET}) was calculated according to the BET equation. The pore size was calculated from the isotherm data by applying the Quenched-Solid Density Functional Theory method (available in the Quantachrome software).

To measure boron concentration, the curcumin method was applied. The Jasco 530 photometer was used for boron analyses [14]. Boron concentration in the feeding solution was 10 mg/L for all experiments.

RESULTS AND DISCUSSION

The evaluated samples were marked as POR150, POR300, POR550, and XAD750 according to their specific surface area. The samples interpolymerized with VBC and DVB were described as CS-POR150, CS-POR300, CS-POR550, and CS-XAD750, and these conjugated with NMGA NCS-POR150, NCS-POR300, NCS-POR550, and NCS-XAD750, respectively. Modification degree, as well as contents of chlorine and nitrogen in the prepared samples, are shown in Table 1.

It is seen that the modification degree was different for small and large particles. It means that the yield of monomers' interpolymerization was larger for samples with low surface area. A similar difference is seen for the Cl to N substitution ratio; chlorine has been replaced by nitrogen with more than 90% for POR150, POR300,

Table 1. Characterization of obtained sorbents

Sample	Particle diameter μm	Modification degree %	Cl content mmol/g	N content mmol/g	Degree of Cl substitution by N %
CS-POR150	100	69.5	1.49	0	0
CS-POR300	100	63.1	0.84	0	
CS-POR550	100	64.6	0.87	0	
CS-XAD750	600	55.7	2.20	0	
NCS-POR150	100	nd*)	0.12	1.39	92.4
NCS-POR300	100		0.06	0.79	92.5
NCS-POR550	100		0.04	0.72	94.5
NCS-XAD750	600		1.63	0.62	38.0

*) – not determined

T a b l e 2. Boron sorption rate constant for evaluated samples

Sample	k_2 mg/(mmolN min)
NCS-POR150	0.0755
NCS-POR300	0.0770
NCS-POR550	0.0802
NCS-XAD750	0.0746

and POR550 samples. In the case of the XAD750 sample, the replacement reached the level of 60%. Hence, when boron sorption would be related to the presence of N-methylglucamine ligand only, the sorption has had to fit the NCS-POR150>NCS-POR300>NCS-POR550>NCS-POR750 series.

The prepared sorbents were designed for use in a sorption-membrane filtration system. Thus, fast sorption kinetic within 30 min of the process was their critical property. The sorption of boron by the evaluated samples did not reflect the order of the NMGA concentration. When the sorption is normalized to 1 mmol of nitrogen (what was adequate to 1 mmol of N-methylglucamine) the following values were obtained: 1.1832 μg/N mmol (for NCS-POR150), 3.5194 μg/N mmol (for NCS-POR300), 1.7579 μg/N mmol (for NCS-POR550), 2.1455 μg/N mmol (for NCS-XAD750).

It was shown previously [11, 14] that boron sorption on sorbents with NMGA ligands followed the pseudo-second-order kinetics

$$\frac{1}{q_t} = \frac{1}{k_2 q_e^2} + \frac{1}{q_e} t$$

where: q_t and q_e are the amounts of adsorbed boron after t and at equilibrium, and k_2 is the adsorption rate constant.

The kinetic studies, when the amount of adsorbed boron was normalized to the content of nitrogen, could indicate the participation of N-methylglucamine ligands in the sorption process. The values of the sorption rate constants are shown in Table 2.

The calculated k_2 values indicate that boron adsorption did not differ for various sorbents. Hence, when sorbents adsorbed various amounts of boron, it had to be another reason for such phenomenon.

Sorbent porosity and pore diameter

Measured surface area and pore diameters are shown in Table 3.

The comparison of the S_{BET} value reveals its decrease after interpolymerization of VBC-DVB. Such results were expected, thus the largest boron sorption for NCS-POR300 sorbent could result from the superposition of NMGA amount and sorbent porous structure.

To check which sorbent property affected boron sorption mostly, three sorbents, namely NCS-POR150, NCS-POR300, and NCS-POR550, were compared. It was assumed that sorption is linearly related to the surface area, pore diameter, and content of the ligand. To make the calculation easier, all variables were normalized considering the possible range of values they could take. Hence, the surface could change from 0 to 100 m²/g, pore diameter from 0 to 50 nm, and NMGA content from 0 to 2.0 mmol/g. The normalization was carried out by the formula:

T a b l e 3. Structure of pristine and modified sorbents

Sample	S_{BET}, m²/g	V_{TOT}, cm³/g	APD, nm
POR150	124.4	1.371	44.1
POR300	369.5	0.806	18.71
POR550	600.0	0.932	6.1
XAD750	765.0	nd	nd
NCS-POR150	<1	0.006	40.1
NCS-POR300	18.9	0.087	18.4
NCS-POR550	70.8	0.140	7.8
NCS-XAD750	392.0	nd	nd

$$(Y_{nor}) = (Y_{run} – Y_{min})/(Y_{max} - Y_{min})$$

where: Y_{nor}, Y_{run}, Y_{min}, and Y_{max} mean normalized, running, minimal and maximal variables.

The set of linear equations, with normalized variables, is shown below

$0.005x_1 + 0.802x_2 + 0.695x_3 = 1.1832$ for NCS-POR150
$0.189x_1 + 0.368x_2 + 0.395x_3 = 3.5194$ for NCS-POR300
$0.708x_1 + 0.156x_2 + 0.360x_3 = 1.7579$ for NCS-POR550

where: x_1 means a surface area, x_2 – pore diameter, and x_3 - contents o NMGA

After calculating the following determinants:

$$D_{matrix} = \begin{matrix} 0.005 & 0.802 & 0.695 \\ 0.189 & 0.368 & 0.395 \\ 0.708 & 0.156 & 0.360 \end{matrix}$$

$$D_{surf} = \begin{matrix} 1.1832 & 0.802 & 0.695 \\ 3.5194 & 0.368 & 0.395 \\ 1.7579 & 0.156 & 0.360 \end{matrix}$$

$$D_{pore} = \begin{matrix} 0.005 & 1.1832 & 0.695 \\ 0.189 & 3.5194 & 0.395 \\ 0.708 & 1.7579 & 0.360 \end{matrix}$$

$$D_{NMGA} = \begin{matrix} 0.005 & 0.802 & 1.1832 \\ 0.189 & 0.368 & 3.5194 \\ 0.708 & 0.156 & 1.7579 \end{matrix}$$

one finds x_1, x_2 and x_3 parameters (the Cramer's method)
$x_1 = D_{surf}/D_{matrix}$, $x_2 = D_{pore}/D_{matrix}$, $x_3 = D_{NMGA}/D_{matrix}$

They are as follows: $x_1 = -46.7$, $x_2 = -131.5$, $x_3 = +153.8$

Based on the calculated parameters, better sorption may be concluded for sorbents having a small pore diameter and a large concentration of N-methylglucamine ligands. What is more, pore diameter and ligand concentration, despite showing opposite effects, have similar absolute values. The effect can be observed in Fig. 1 where boron removal for the investigated sorbents is compared.

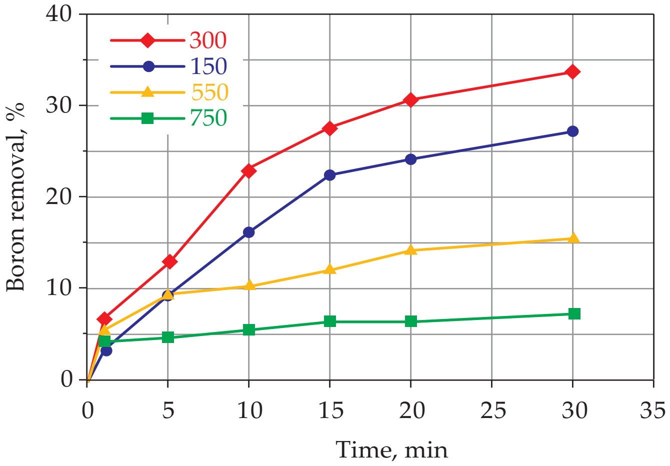

Fig. 1. Boron removal kinetics for evaluated samples (to simplify NCS-POR150, NCS-POR300, NCS-POR550 and NCS-XAD750 are shown as 150, 300, 550 and 750)

Among three compared sorbents the fastest kinetics of boron sorption is observed for NCS-POR300 sample. That one should be used for boron separation in the hybrid process.

CONCLUSIONS

The performed studies evaluated the effects of the ligand amount and pore structure on sorption properties of core-shell particles, designated for a hybrid system. The use of the core matrices with different porous structures resulted in the synthesis of efficient sorbent for the boron removal from diluted solutions. The detailed studies reviled two important properties of the obtained sorbents: contents of N-methyl glutamine and pore diameter. Among the tested Poropak matrices, the best sorbent was obtained by the use of matrix Poropak with a surface of 300 m^2/g. This material is recommended for the hybrid system.

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