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Cross-linked polysaccharide konjac glucomannan: synthesis, characterization and phenol adsorption

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New polymeric adsorbents based on water soluble polysaccharide konjac glucomannan cross-linked with blocked alkyl- and aryl-, di- or polyisocyanate were synthesized and used for phenol adsorption from aqueous solutions. The interaction of polysaccharide with e-caprolactam blocked isocyanates was confirmed by pyrolysis mass-spectrometry. Glycopolymers based on cross-linked konjac glucomannan demonstrate good phenol sorption ability. To describe phenol adsorption on glycopolymers Langmuir and Freundlich models were used. The influence on phenol adsorption capacity of polysaccharide hydroxyl group substitution degree, isocyanate structure as well as pH value was analyzed. Adsorption equilibrium had been reached after 24 hours contact with phenol, nevertheless, 75–80% of phenol is adsorbed during first 6–8 hours. The highest phenol adsorption capacity onto GP had been reached at neutral medium whereas adsorption capacities at acid and alkali media are slightly lower. In contrast to glycopolymers based on aliphatic diisocyatate glycopolymers based on aromatic ones show higher adsorption capacity. This indicates the important role of π–π interactions between aromatic rings of adsorbate and polymeric matrix during adsorption.

Keywords: phenol adsorption, glycopolymers, konjac glucomannan, blocked isocyanates, adsorption isotherm.

Introduction.

Water pollutant due to organic compounds, in particular phenol, remains a serious environmental problem. Among the different organic pollutants in wastewater, phenols are considered as priority pollutants since they are harmful to plants, animals and human, even at low concentrations.

A number of methods such as coagulation, filtration with coagulation, precipitation, ozonation, adsorption, ion exchange, reverse osmosis and advanced oxidation processes have been used for the removal of organic pollutants from polluted water and wastewater. Among the possible techniques for water treatments, the adsorption process by solid adsorbents shows potential as one of the most efficient methods for the treatment and removal of organic contaminants in wastewater treatment. Adsorption has advantages over the other methods because of simple design and can involve low investment in term of both initial cost and land required [1–3].

Natural materials, in many instances are relatively cheap, abundant in supply and have significant potential for modification and ultimately enhancement of their adsorption capabilities [4, 5].

In this paper, adsorbents, glycopolymers (GP) based on plant polysaccharide konjac glucomannan cross-linked with blocked alkyl- or aryl-,di- or polyisocyanate were synthesized and used for phenol adsorption from water solutions. The influence of isocyanate structure and functionality, hydroxyl group substitution degree, phenol concentration and solution pH on the GP adsorption capacity was investigated.

Materials and methods.

Materials.

Plant polysaccharide konjac glucomannan produced from Amorphophallus konjak root (Chengdu Root Industry Co., Ltd. Sichuan, China) 120–200 mesh and e-caprolactam (Sigma Aldrich) were used without prior purification. Polymethylenepolyphenyl isocyanate (Dow) was used as supplied.

Hexamethylene-1,6-disocyanate (Sigma Aldrich) T_b= 82–85 °C/0,1 mm Hg and tolylene diisocyanate (Sigma Aldrich) 80/20 mixture of the 2,4- and 2,6-isomer, T_b= 115–120 °C/10 mm Hg, 4,42 -methylenebis(phenyl isocyanate) T_b= 200 °C/5 mm Hg, T_{melt}=42-45 °C, were distilled under vacuum

The blocked di- and polyisocyanates (BIC): tolylene diisocyanate (TDI), hexamethylene-1,6-diisocyanate (HDI), 4,42 -methylenebis (phenyl isocyanate) (MDI) and polyisocyanate(PIC) blocked by e-caprolactam (CL) further referred to as TDI-CL, HDI-CL, MDI-CL, and PIC-CL, respectively, were synthesized to cross-link the konjac glucomannan.BIC can release reactive NCO-group under heating [6].

The structure of obtained BIC was identified by FTIR and ^{1}H NMR spectroscopy. Their deblocking temperature was determined using thermogravimetry and pyrolytic mass-spectrometry methods [6].

Sample preparation.

Glycopolymers based on polysaccharide KGM and various BIC with hydroxyl group substitution degree of 40 and 80%were obtained via the interaction of KGM with BIC at 150 °C. The obtained glycopolymers are further referred to as GP(TDI-CL), GP(HDI-CL), GP(MDI-CL), and GP(PIC-CL).The reaction was carried out during 30 minutes in heterogeneous condition in the melt of BIC on polysaccharide surface. The powdered polymer systems were obtained.

Methods.

Pyrolysis mass-spectrometry method was used to confirm the interaction of KGM with BIC. The mass-spectra were recorded on MS-instrument that consists of linear pyrolysis cell (temperature range from 25 to 400 °C) and mass-spectrometer MX–1321 allowing determination of the components of gas mixture in the mass number range of 1–4000.

Phenol adsorption from aqueous solution on GP samples was carried out at room temperature (20±2 °C) at different pH in static conditions during 7 days with initial defined phenol concentration C_o (from 0,6 to 50 mg/l). The adsorption process was controlled by electron spectroscopy in UV region following of characteristic phenol band intensity at 260 nm. Alteration of phenol concentration in solution during the adsorption process was determined according to calibration plot.

Glycopolymer adsorption capacity (*A*) to phenol was calculated using following equation:

$$A = \frac{(C_0 - C) \cdot V}{m}, \tag{1}$$

where C_0 and C are the initial and equilibrium concentrations of phenol, respectively, mg/l; V is the solution volume, l; m is the mass of the glycopolymer film used, g.

Results and Discussion.

Interaction of konjac glucomannan with blocked icosyanates.

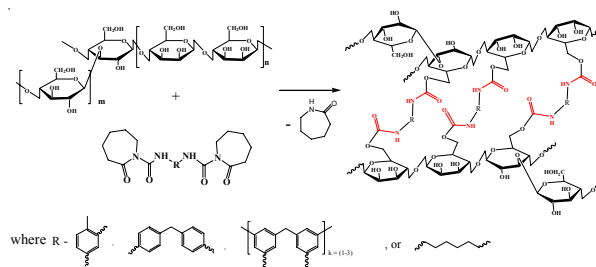The scheme of KGM interaction with BIC is shown below:

Figure 1 represents mass-spectra of TDI-CL and GP(TDI-CL). Figure 2 demonstrates significant difference between experimental temperature dependence GP(TDI-CL) and additive ion current curve of initial reagents taken in the same ratio as in GP(TDI-CL).

According to Figure 1 the reduction of number and types of pyrolytic decomposition fragments on mass-spectra of GP(TDI-CL) compared with TDI-CL at the same temperature are observed. For example, the number of decomposition fragments at 150 °C reduces from 58 for TDI-CL to 29 for GP(TDI-CL). That indicates the binding of TDI to the polysaccharide. According to our previous research [6] this temperature (150 °C) relates to releasing of reactive NCO-group in thermal dissociation process.

As it can be seen the significant difference between additive and experimental curves indicates chemical interaction of KGM and TDI. In particular temperature dependence of ion current intensity of GP(TDI-CL) has two well-divided maxima at 185 °C and 240 °C whereas additive curve possesses four maxima at 115, 180, 265, and 350 °C.

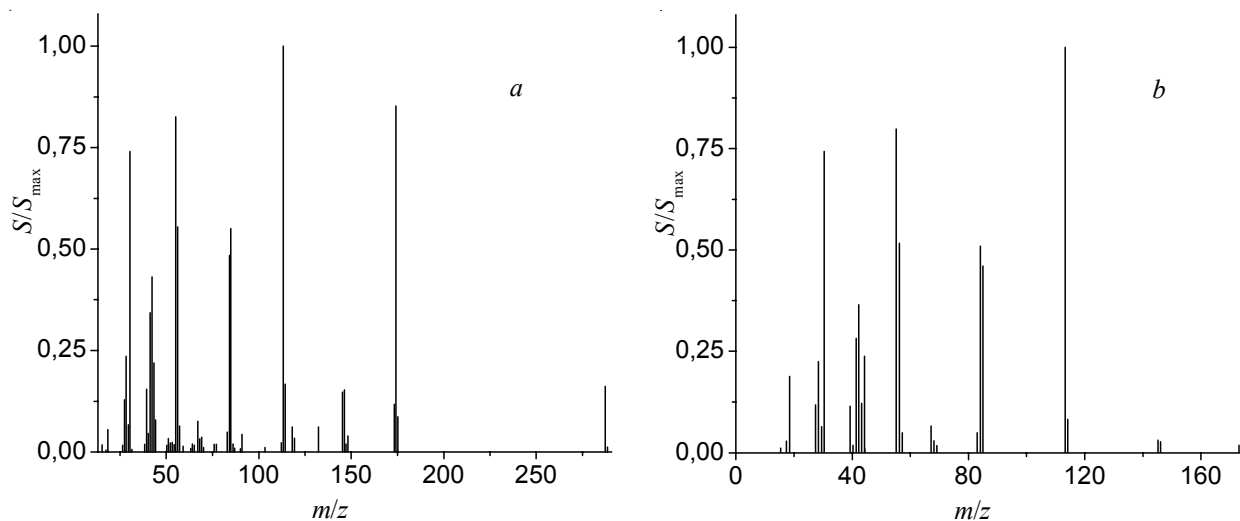The maximum of ion current intensity at 240 °C for

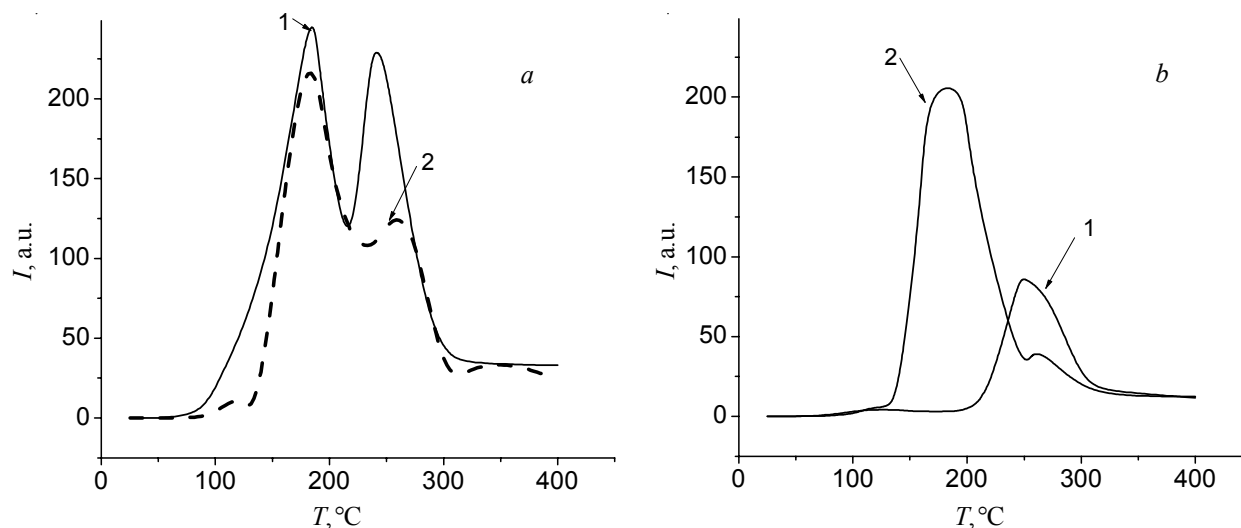Fig. 1. Mass-spectra of TDI-CL (*a*) and GP(TDI-CL)-40 (*b*) at 150 °C

Fig. 2. Ion current temperature dependence of pyrolytic decomposition: *a* – GP(TDI-CL)-40 experimental (*1*) and additive (*2*) curves; *b* – KGM (*1*) and TDI-CL(*2*)

GP(TDI-CL) as well as qualitative and quantitative composition of fragments is typical for KGM decomposition. The maximum contribution to the intensity of the ion current GP at this temperature are fragments with mass numbers 18 and 44, corresponding to water and carbon dioxide. However the appearance at this temperature of some additional fragments characteristic for TDI-CL pyrolysis may indicate a decomposition of urethane component in GP formed due to interaction of KGM with TDI. The maximum of ion current for GP at 150 °C can be related with presence of TDI in the polymer system. However the number and types of pyrolytic decomposition fragments at this maximum for GP has a significant difference compared with TDI.

In addition, it was shown earlier for GP(PIC-CL) that relative intensity of such two maxima correlates with cal-

culated substitution degree of KGM hydroxyl group [7].

Adsorption of phenol on GP based on various isocyanates.

The kinetic curves of phenol adsorption onto glycopolymers based on different BIC at various medium pH are shown at Figure3.

Glycopolymers based on cross-linked konjac glucomannan demonstrate good adsorption ability for phenol. According to kinetic data (Figure 3*a*) adsorption equilibrium had been reached after 24 hours contact with phenol solution for GP based on PIC-CL, HDI-CL, and MDI-CL. For GP(TDI-CL) adsorption equilibrium remained unchanged after 48 hours. However, most part of phenol (75–80 %) is adsorbed during first 6–8 hours.

The highest phenol adsorption capacity onto GP had been reached at neutral medium whereas adsorption at
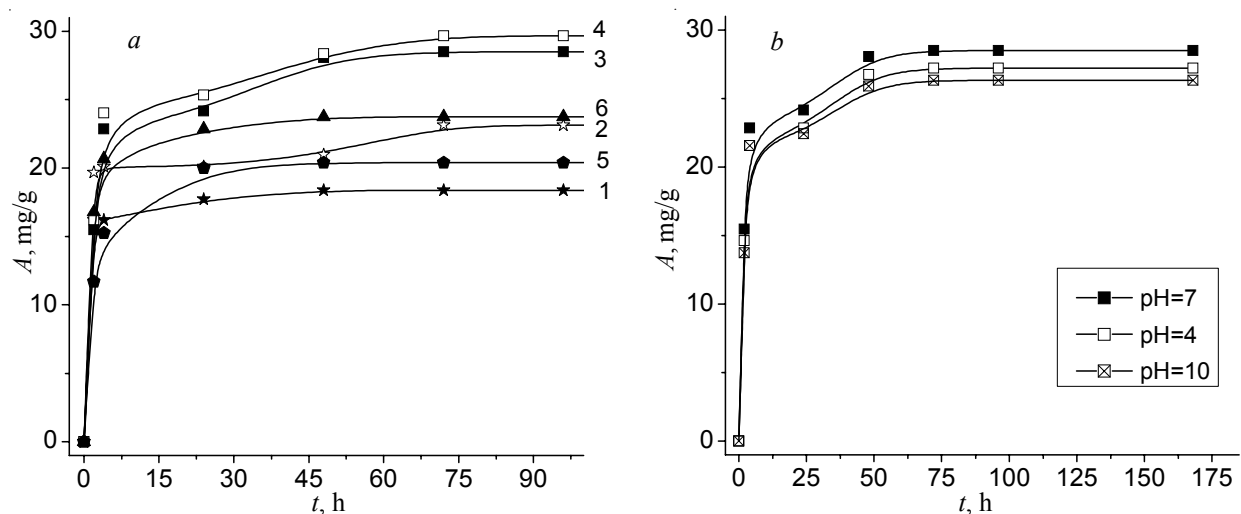

Fig. 3. The kinetic curves of phenol adsorption onto glycopolymers based on different BIC (*a*) and at various pH medium on GP(TDI-CL)-40 (*b*): *1* – GP(PIC-CL)-40; *2* – GP(PIC-CL)-40; *3* –GP(TDI-CL)-40; *4* – GP(TDI-CL)-80; *5* – GP(HDI-CL)-40; *6* – GP(MDI-CL)-40

Table. Constants and correlation coefficients of Langmuir and Freundlich equations

GP	Langmuir			Freundlich		
	A_{max}, mg/g	$K_L \cdot 10^2$, l/mol	R^2	$1/n$	$\lg K_F$	R^2
GP(PIC-CL)-40	17,90	1,9	0,999	1,05	-0,42	0,999
GP(PIC-CL)-80	25,44	1,7	0,999	1,02	-0,32	0,995
GP(TDI-CL)-40	23,26	9,0	0,999	1,05	-0,30	0,998
GP(TDI-CL)-80	27,70	3,5	0,999	1,06	-0,35	0,998
GP(MDI-CL)-40	31,17	1,2	0,999	0,91	-0,36	0,999
GP(MDI-CL)-80	29,80	1,4	0,999	0,95	-0,37	0.997
GP(HDI-CL)-40	15,20	1,9	0,999	0,98	-0,49	0,998
GP(HDI-CL)-80	18,52	1,3	0,999	1,03	-0,59	0,998

acid and alkali media slightly decreased (Figure 3b). Thus, further experiments conducts at neutral medium.

In this study, adsorption of phenol onto GP based on KGM cross-linked with different BIC was described with both Langmuir and Freundlich models according to equation (2) and equation (3), respectively:

$$\frac{C}{A} = \frac{C}{A_{max} K_L} + \frac{1}{A_{max}}, \qquad (2)$$

$$\lg A = \lg K_F + \frac{1}{n} \lg C, \qquad (3)$$

where K_L is the Langmuir isotherm constant related to the energy or net enthalpy, A_{max} is the maximum adsorption capacity (mg/g), and K_F is the Freundlich constant related to the adsorption capacity, and n is the constant related to energy surface heterogeneity.

The linear plot obtained from C/A against C with correlation coefficients R^2 greater than 0,99, indicates that the adsorption isotherm can be described by Langmuir model.

Values of K_F and n can be evaluated by plotting log A against log C. The calculated Langmuir and Freundlich parameters are shown in Table.

According to data presented in Table both Langmuir and Freundlich adsorption isotherm models can be used to describe phenol adsorption onto GP. This is evidenced by close to 1 values of the correlation coefficient R^2. The highest adsorption capacity is observed for GP(MDI-CL)-40 and GP(HDI-CL)-40 has the lowest value.

In general, phenol adsorption onto sorbents based on polysaccharides occurs by hydrophobic interaction, hydrogen bonding and p–p interactions. Adsorption capacity of GP based on aromatic diisocyatates is higher then of GP based on aliphatic diisocyanate that can indicate that π-π interactions between aromatic rings of adsorbate and polymeric matrix play an important role in adsorption of phenolic compounds on GP [8, 9]. This correlates with the growth of the sorption capacity of GP based on PIC-CL and TDI-CL with increasing of the polysaccharide hydroxyl groups substitution degree. The influence of the hydroxyl groups substitution degree on the change in adsorption capacity of GP(HDI-CL) and GP(MDI-CL) requires additional investigation.

Freundlich isotherm parameters K_F listed in Table stay almost unchanged with a change in the structure of the isocyanate and indicate that active sites for all GP have similar strength. The decreases of $1/n$ for GP based on MDI-CL and HDI-CL might be regarded as increased surface heterogeneity.

Conclusion.

A study of the phenol adsorption features on GP based on the plant polysaccharide konjac glucomannan and blocked isocyanates of various structure showed that cross-linked KGM demonstrates good adsorption ability for phenol. Phenol adsorption onto GP is little affected by pH. Adsorption equilibrium in neutral medium is achieved in 24–48 hours; however, 75–80 % of phenol is adsorbed during first 6–8 hours.

Both Langmuir and Freundlich adsorption isotherm models were used to describe phenol adsorption on GP with correlation coefficient R^2 values close to 1. Structure of isocyanate and KGM group substitution degree can influence on phenol removal efficiency. The higher adsorption capacity of GP based on aromatic diisocyatates indicates important role of p-p interactions between aromatic rings of adsorbate and polymeric matrix.

References

1. *Valderrama C., Barios J., Farran A. J. CortinaL.* Evaluation of Phenol/Aniline (Single and Binary) Removal from Aqueous Solutions onto Hypercross-linked Polymeric Resin (Macronet MN200) and Granular Activated Carbon in Fixed-Bed Column. Water Air Soil Pollut. 2011 Feb; 215(1-4): 285-97. Available from: https://doi.org/10.1007/s11270-010-0478-x

2. *Abussaud B., Asmaly H., Saleh A. Gupta K., Laoui T., Atieh M.A.* Sorption of phenol from waters on activated carbon impregnated with iron oxide, aluminum oxide and titanium oxide. J. Molec. Liq. 2016 Jan; 213: 351-9. Available from: https://doi.org/10.1016/j.molliq.2015.08.044

3. *Canizares P., Lobato J., Garcэa-Gomez J., Rodrigo M.A.* Combined adsorption and electrochemical processes for the treatment of acidic aqueous phenol wastes. J. Appl. Electrochem. 2004 Jan; 34(1): 111-7.

Available from: https://doi.org/10.1023/B:JACH.0000005607.37738.71

4. *Crini G.* Recent developments in polysaccharide-based materials used as adsorbents in wastewater treatment. Prog. Polym. Sci. 2005Jan; 30(1): 38-70. Available from: https://doi.org/10.1016/j.progpolymsci.2004.11.002

5. *Crini G.* Non-conventional low-cost adsorbents for dye removal: A review. Biores. Technol. 2006 Jul;97(9): 1061–85Available from: https://doi:10.1016/j.biortech.2005.05.001

6. *Didenko K.S., Kozak N.V., Bortnytskyi V.I., Komliakova O.M., Klepko V.V., Rukhailo M.V.* The influence of structure and functionality of e-caprolactam blocked isocyanates on their thermal properties. Ukrainian Chemical Journal.2016; 82(8): 110-6.

7. *Kozak N.V., Didenko K.S., Dmytriieva T.V., Bortnytskyi V.I.* The interaction of the blocked polyisocyanate with konjac glucomannan. Ukrainian Chemical Journal.2014; 80(8):119-23.

8. *Li J.-M., Meng X.-G., Hu C.-W., Du J.* Adsorption of phenol, *p*-chlorophenol and *p*-nitrophenol onto functional chitosan. Biores. Technol. 2009 Feb; 100(3): 1168-73. Available from: https://doi.org/10.1016/j.biortech.2008.09.015

9. *Didenko K., Kozak N., Klepko V.* Preparation and characterization of phenol sorbents based on konjac glucomannan and water-soluble blocked isocyanates. Chem. and Chem. Tech. 2017. 11(3): 270-276. Available from: https://doi.org/10.23939/chcht11.03.270

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Зшитий полісахарид конжак глюкоманан: синтез, характеристики й адсорбція фенолу

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Синтезовано нові полімерні адсорбенти на основі водорозчинного полісахариду конжак глюкоманану, зшитого блокованими алкільними і арильними ди- або поліізоціанатами, для сорбції фенолу з водних розчинів. Методом піролітичної мас-спектрометрії підтверджено взаємодію полісахариду з блокованими ізоціанатами. Глікополімери на основі зшитого конжак глюкоманану проявляють хороші сорбційні властивості щодо фенолу. Для опису адсорбції фенолу глікополімерами було використано моделі Ленгмюра і Фрейндліха. Розглянуто вплив на адсорбійну ємність отриманих глікополімерів ступеня заміщення гідроксильних груп полісахариду, структури ізоціанату і pH середовища. Глікополімери на основі ароматичних діізоціанатів проявляють вищу сорбійну здатність порівняно з глікополімерами на основі аліфатичних діізоціанатів. Це вказує на роль π-π взаємодії між ароматичними кільцями адсорбату і полімерною матрицею у процесі адсорбції.

Ключові слова: адсорбція фенолу, глікополімери, конжак глюкоманан, блоковані ізоціанати, ізотерма адсорбції.

Сшитый полисахарид конжак глюкоманнан: синтез, характеристики и адсорбция фенола

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Синтезированы новые полимерные адсорбенты на основе водорастворимого полисахарида конжак глюкоманнана, сшитого блокированными алкильными и арильными ди- и полиизоцианатами, для сорбции фенола из водных растворов. Методом пиролитической масс-спектрометрии подтверждено взаимодействие полисахарида с блокированными изоцианатами. Гликополимеры на основе сшитого конжак глюкоманнана проявляют хорошие сорбционные свойства относительно фенола. Для описания адсорбции фенола гликополимерами использованы модели Ленгмюра и Фрейндлиха. Рассмотрено влияние на адсорбционную емкость полученных гликополимеров степени замещения гидроксильных групп полисахарида, структуры изоцианата и pH среды. Гликополимеры на основе ароматических диизоцианатов проявляют более высокую адсорбционную способность по сравнению с гликополимерами на основе алифатических диизоцианатов. Это указывает на роль π-π взаимодействия между ароматическими кольцами адсорбата и полимерной матрицей в процессе адсорбции.

Ключевые слова: адсорбция фенола, гликополимеры, конжак глюкоманнан, блокированные изоцианаты, изотерма адсорбции.