

PREPARATION AND CHARACTERIZATION OF PHENOL SORBENTS BASED ON KONJAC GLUCOMANNAN AND WATER-SOLUBLE BLOCKED ISOCYANATES

Kateryna Didenko¹, Natalia Kozak¹, Valerii Klepko¹*

https:

Abstract.¹ In this work water-soluble blocked alkyl- or aryl-diisocyanate and glycopolymers based on konjac glucomannan and the blocked diisocyanate were synthesized and characterized. Their phenol sorption ability has been studied. Adsorption experiments were carried out to evaluate the effects of structure of isocyanate, polysaccharide hydroxyl group substitution degree, solution pH, contact time, on the phenol removal efficiency. Langmuir and Freundlich models were applied to describe the adsorption isotherms of phenol, and adsorption parameters were evaluated. The determined values of adsorption capacities vary from 12.8 to 25.0 mg/g depending on diisocyanate structure and polysaccharide group substitution degree. It was shown that neutral and weakly alkali mediums are favourable for phenol adsorption by the new glycopolymers.

Keywords: blocked isocyanate, polysaccharide, konjac glucomannan, phenol adsorption, adsorption isotherm.

1. Introduction

Phenolic compounds are present in wastewaters arising from a variety of industries (including olive mills, oil refineries, plastics, and leather, and paint, pharmaceutical and steel industries). As it is known, these compounds are toxic, even at low concentrations. Therefore a previous treatment of the water is required to discharge the effluents to the environment. In appropriate circumstances, the phenolic compounds contained in wastewaters can be economically recovered. The two best methods to treat these wastes are their destruction by chemical oxidation techniques or by adsorption [1-8]. It should be noted that adsorption is more preferable due to its potential to remove both organic and inorganic constituents, even at low concentrations.

Numerous approaches have been studied for the development and investigation of cheap and effective adsorbents based on natural polymers. Also, it is well known that polysaccharides have a good capacity to associate *via* chemical and physical interaction with a wide variety of molecules. Such polysaccharides as chitin, chitosan, starch, cellulose deserve attention as effective adsorbents due to their particular structure, physico-chemical characteristics, chemical stability, and high reactivity [9]. Moreover, the presence of chemical active groups, such as hydroxyl, acetamide, amino functions, leads to high selectivity of polysaccharides towards aromatic compounds. Thus adsorption on polysaccharides and their derivatives, including cross-linked polysaccharides, can be used in wastewater treatment for extraction and separation of organic compounds such as phenol.

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

2. Experimental

2.1. Materials and Reagents

Hexamethylene-1,6-disocyanate (Sigma Aldrich), $T_b = 355\text{--}358\text{ K}/0.13\text{ kPa}$ and tolylene diisocyanate (Sigma Aldrich) 80/20 mixture of 2,4- and 2,6-isomer, $T_b = 388\text{--}393\text{ K}/13\text{ kPa}$, were distilled under vacuum.

Polysaccharide konjac glucomannan produced from *Amorphophallus konjac* root (Chengdu Root Industry Co., Ltd. Sichuan, China) 120-200 mesh; ϵ -Caprolactam (CL) and sodium hydroxide were used without prior purification.

¹ Institute of Macromolecular Chemistry NAS of Ukraine,
48, Kharkivske Hwy., 02160 Kyiv, Ukraine
* didenko.katherina@gmail.com

© Didenko K., Kozak N., Klepko V., 2017

2.2. Synthesis of Water-Soluble Blocked Isocyanates

The water-soluble blocked diisocyanates (BIC): tolylene diisocyanate (TDI) and hexamethylene-1,6-diisocyanate (HDI) blocked by a sodium salt of amino-hexanoic acid (TDI-ACA and HMDI-ACA, respectively) were synthesized to cross-link the konjac glucomannan.

These water-soluble blocked diisocyanates were obtained in two stages. At the first stage sodium salt of aminocaproic acid (ACA) was synthesized by CL hydrolysis. At the second stage the blocking reaction of diisocyanate (TDI or HMDI) by sodium salt of aminohexanoic acid (ACA) was carried out at 291 K for 2 h in ACA aqueous solution.

The reaction products can release reactive NCO-group under heating [10].

The structure of obtained products was identified by FTIR and ^1H NMR spectroscopy.

FTIR spectra were recorded using TENSOR 37 spectrometer (Bruker) in the frequency region from 400 to 4000 cm^{-1} . ^1H NMR spectra were recorded using Varian GEMINI 2000 spectrometer with a proton resonance frequency of 400 MHz at 293 K in a deuterium water.

2.3. Preparation of Glycopolymers

Weighed KGM and BIC were dissolved in water separately. Then dissolved in water KGM was mixed with a solution of BIC at room temperature to form hydrogel. Due to water solubility of the reagents mixing of KGM with TDI-ACA or HMDI-ACA in the common solvent allows obtaining their most homogeneous mixture. Then it allows obtaining the glycopolymers in the form of a film. The polysaccharide cross-linking reaction was carried out at 160°C for 30 min. To avoid reaction of released isocyanate groups with water, the reaction mixture was dried at the temperature of 373 K, and then the temperature was raised to 433 K [10]. Samples were obtained in the form of thin porous film.

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 liner pyrolysis cell (temperature range from 298 to 673 K) and mass-spectrometer MX-1321 allowing determination of the components of gas mixture in the mass number range of 1–4000.

2.4. Phenol Adsorption on Glycopolymers

Phenol adsorption from the aqueous solution by glycopolymer samples was carried out at room temperature (293 ± 2 K) at different pH in static conditions during 7 days with initial defined concentration C_0 (from 0.6 to 50 mg/l). The adsorption process was controlled by the electron spectroscopy in UV region analyzing the characteristic phenol band intensity at 260 nm. Alteration of phenol concentration in solution during the adsorption process was determined according to the calibration plot.

Glycopolymers adsorption capacity (A) to phenol was calculated using the following equation:

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

where C_0 and C – the initial and final concentrations of phenol, respectively, mg/l; V – the solution volume, l; m – the weight of the glycopolymer film used, g.

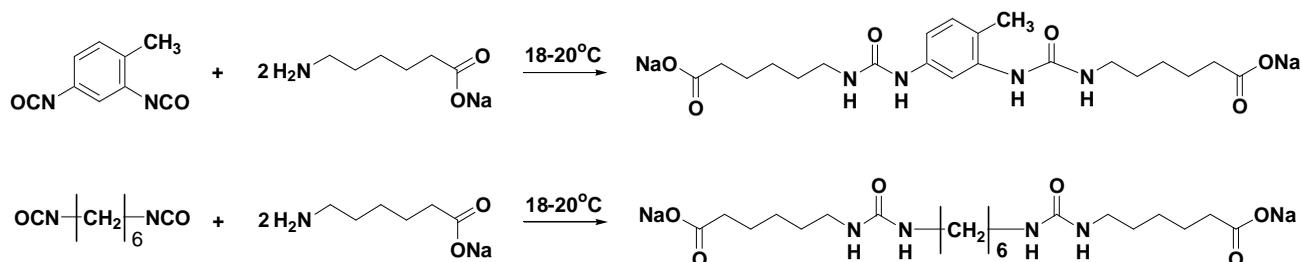
3. Results and Discussion

3.1. Water-Soluble Blocked Isocyanates

The interaction of ACA with diisocyanate leads to the formation of blocked diisocyanate (see scheme) with the output of 95 %. The obtained blocked diisocyanates are yellow coloured powder with $T_{diss} = 423\text{--}428$ K.

FTIR and ^1H NMR spectra of the BIC are presented in Figs.1 and 2, respectively.

According to FTIR data absorption at 3315, 1640 and 1565 cm^{-1} corresponds to the stretching vibrations of NH, carbonyl (C=O), and bending vibrations of NH, respectively. Absorption band at 2274 cm^{-1} is not observed indicating that the $-\text{NCO}$ groups of diisocyanates are completely blocked by ACA.



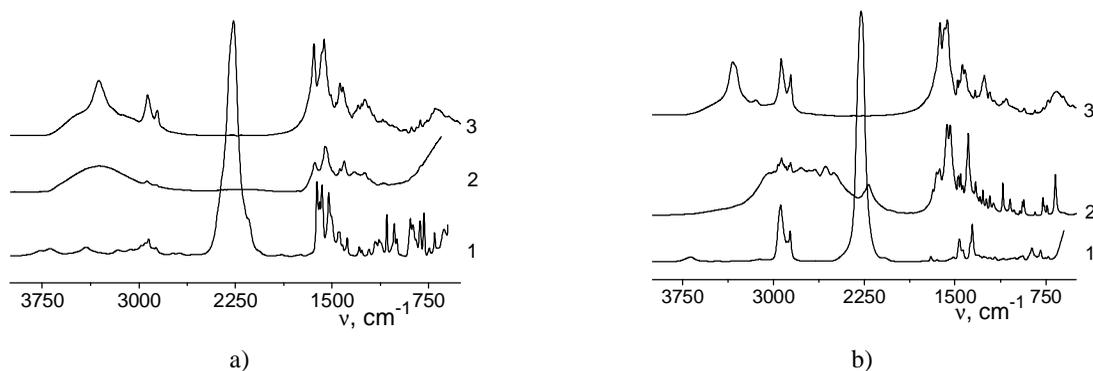


Fig. 1. FTIR-spectra of initial reagents (diisocyanate (1), sodium salt of aminocaproic acid (2) and blocked isocyanate (3) based on TDI (a) and HDI (b))

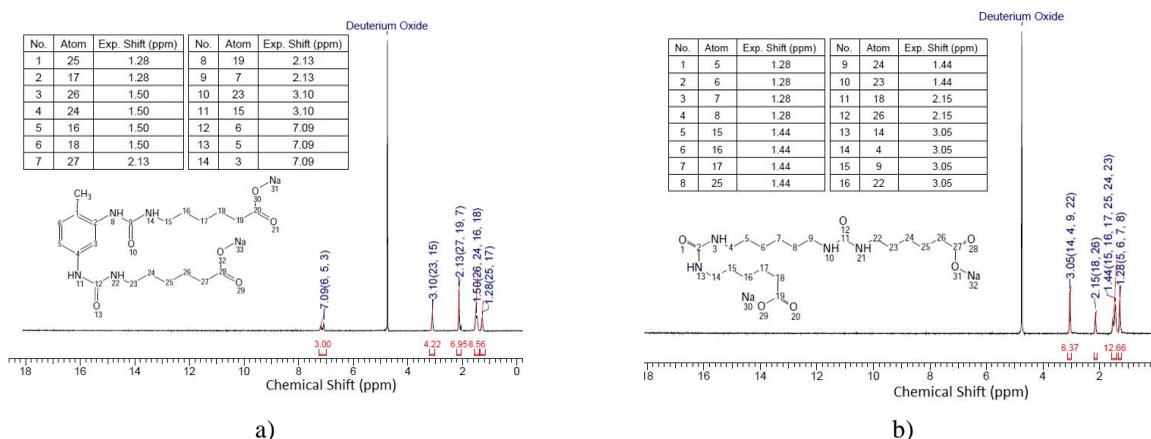


Fig. 2. ^1H NMR spectra of blocked diisocyanates based on TDI (a) and HDI (b)

^1H NMR spectrum of TDI-ACA has a singlet in the region of 3.10 ppm that corresponds to protons 15, 23 in $-\text{CH}_2-\text{NH}-$. Chemical shift of 7.09 ppm relates to protons in the aromatic ring (3, 5, 6). The singlet of 2.13 ppm refers to protons in the methyl group (27) and in $-\text{CH}_2-\text{COOR}$ (7, 19, 27). The proton signals in $-\text{CH}_2-$ group of ACA (16, 17, 18, 24, 25, 26) are present in regions of 1.28 and 1.50 ppm.

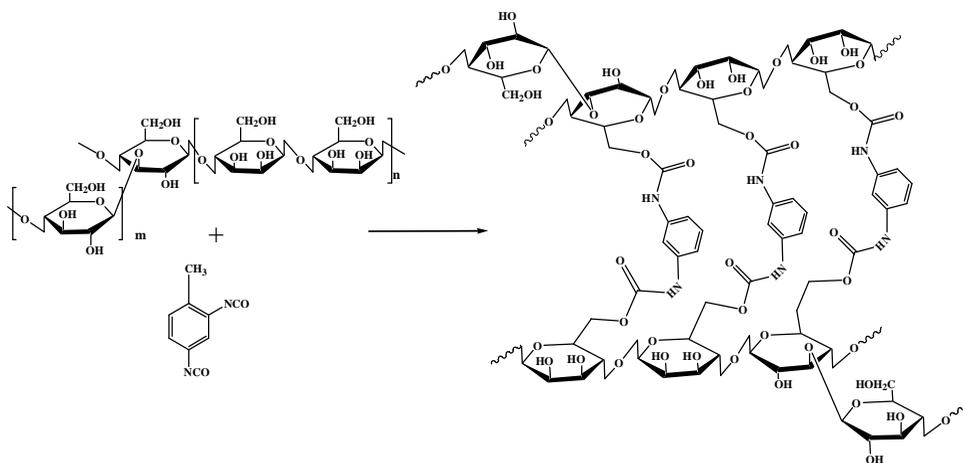
^1H NMR spectrum of HDI-ACA has a singlet in the region of 3.05 ppm that relates to protons in $-\text{CH}_2-\text{NH}-$ (4, 9, 14, 22). Protons in $-\text{CH}_2-\text{COOR}$ (18, 26) give singlet at

2.15 ppm. The proton signals in $-\text{CH}_2-$ group of ACA (5, 6, 7, 8, 15, 16, 17, 23, 24, 25) are present at 1.28 and 1.44 ppm.

FTIR and ^1H NMR spectra confirm the formation of BIC.

3.2. Binding of Diisocyanates with Polysaccharide during Crosslinking

The interaction of KGM with BIC is shown in the scheme below:



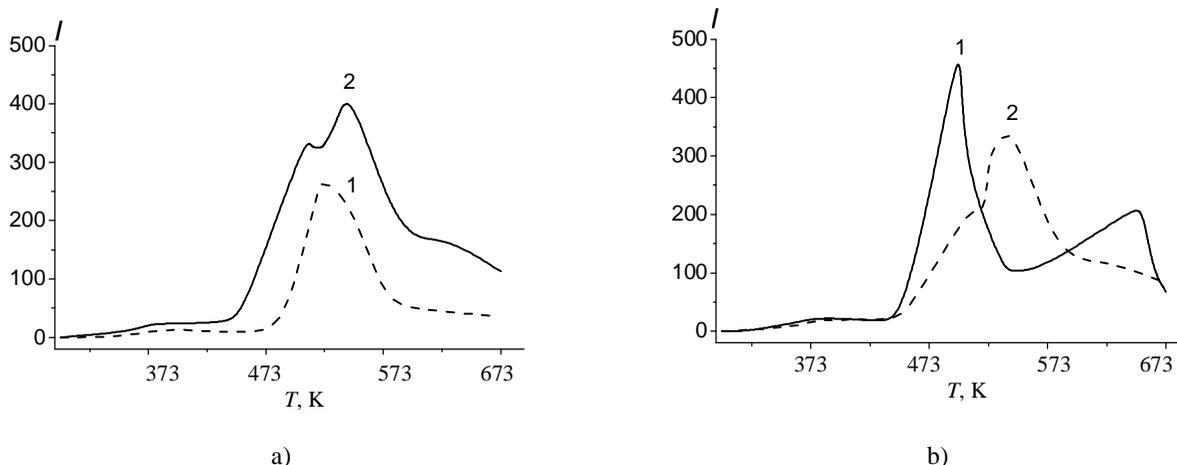


Fig. 3. Temperature dependence of initial components (a) and GP (b) ion current.
For (a): 1 – KGM, 2 – TDI-ACA (2); for (b): 1 – experimental curve, 2 – additive curve

The thermal properties (temperature dependence of intensity and composition of ion current, analysis of ionic fragments of PGU pyrolytic decomposition) of glycopolymers and initial reagents were investigated by a pyrolysis mass-spectrometry. Temperature dependence of initial reagents and glycopolymers ionic current are shown in Fig. 2. According to mass-spectrometry data the significant difference between experimental and additive ion current curves is observed (Fig. 3 b). In contrast to the additive curve the experimental temperature dependence of ion current for GP has two well-divided maxima at 498 and 648 K. These maxima do not correspond to the maxima of ion current of initial reagents. The stage of GP pyrolytic decomposition with maximum ion current at 498 K can be related to the presence of TDI in the system. However, the characteristics of ion current at this stage for GP and TDI-ACA are significantly different. The ion current intensity as well as the number and types of ionic fragments of GP pyrolytic decomposition decrease in comparison with analogous stages of TDI pyrolytic decomposition from 47 to 30. The number and type of ion fragments at 648 K for glycopolymer were similar to KGM decomposition fragments at 523 K.

The decrease of ion current intensity, the reduction of number and types of ionic fragments of GP pyrolytic decomposition in the temperature region common to decomposition of TDI-ACA refer to binding of TDI with polysaccharide during cross-linking with the formation of thermostable structures.

3.3. Effect of the Contact Time of Glycopolymers with Phenol on Phenol Adsorption

The kinetic curves and phenol adsorption isotherm onto glycopolymers are shown in Fig. 4.

According to Fig. 4a adsorption equilibrium for glycopolymer samples was reached after 48h contact with a phenol solution. It should be noted that 65 % of phenol had been adsorbed for the first 4–6 h.

As it can be seen glycopolymers based on cross-linked konjac glucomannan exhibit good adsorption ability for phenols.

In this study, adsorption of phenol onto GP based on KGM cross-linked with TDI-ACA or HDI-ACA was described with both Langmuir and Freundlich models according to Eqs. (2) and (3), respectively:

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

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

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

Experimental results show that a linear plot is obtained from C/A versus C . All linear correlation coefficients R^2 are greater than 0.99, indicating that the adsorption isotherm can be described by the Langmuir model. The calculated Langmuir parameters are shown in Table.

Values of K_F and n can be evaluated by plotting $\log A$ against $\log C$. Experimental results show that all linear correlation coefficients R^2 are greater than 0.98, indicating that the adsorption isotherm of phenols can be described also with the Freundlich model. The calculated value of n and K_F are shown in Table.

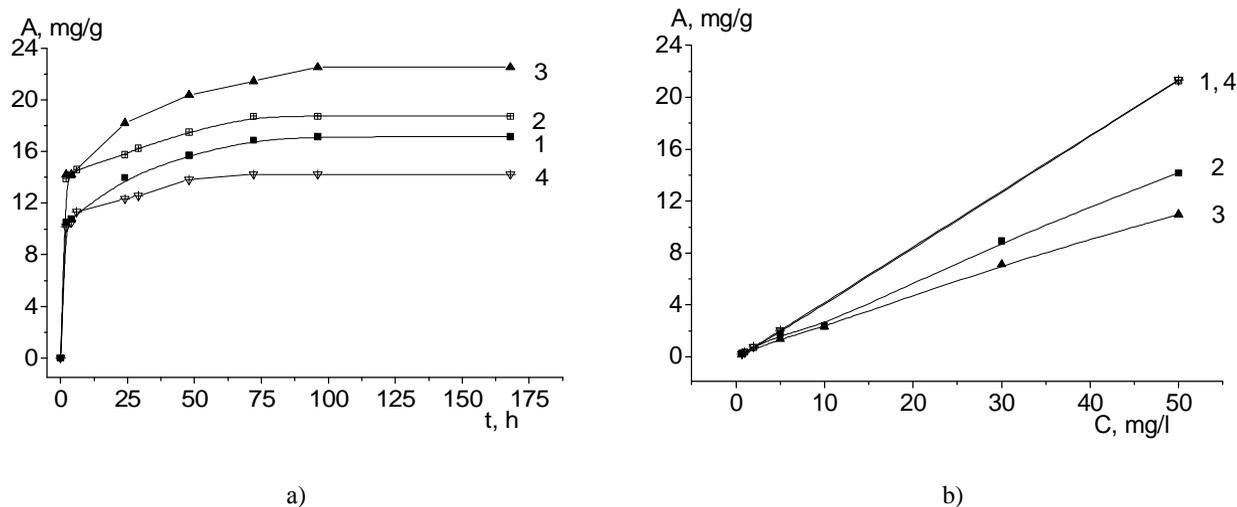


Fig. 4. The kinetic curves (a) ($m = 0.07$ g, $[\text{PhOH}] = 0.05\text{M}$, $\text{pH} = 7$) and isotherms of phenol adsorption (b) ($t = 48$ h, $m = 0.07$ g, $\text{pH} = 7$) onto glycopolymers: GP(TDI)-40 (1); GP(TDI)-80 (2); GP(MDI)-40 (3) and GP(MDI)-80 (4)

Table

Constants and correlation coefficients of Langmuir and Freundlich equations

GP	Langmuir			Freundlich		
	A_{max} , mg/g	K_L , l/mol	R^2	$1/n$	$\lg K_F$	R^2
GP(TDI)-40	20.0	$1.8 \cdot 10^{-2}$	0.999	0.94	-0.5	0.997
GP(TDI)-80	25.0	$1.2 \cdot 10^{-2}$	0.999	0.83	-0.08	0.988
GP(HDI)-40	20.8	$1.8 \cdot 10^{-2}$	0.999	1	-0.43	0.999
GP(HDI)-80	12.8	$2.7 \cdot 10^{-2}$	0.998	1	-0.44	0.999

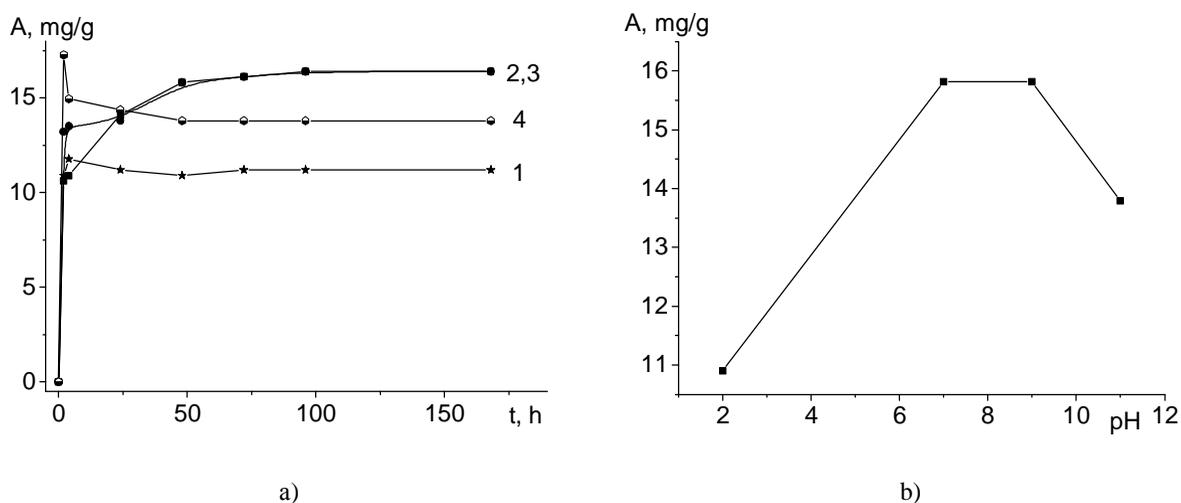


Fig. 5. Phenol adsorption onto GP(TDI)-40: effect of pH on adsorption equilibrium (a); pH influence on adsorption capacity ($t = 24$ h, $m = 0.07$ g, $[\text{PhOH}] = 0.05\text{M}$, $\text{pH} = 7$) (b). 1 – $\text{pH} = 2$; 2 – $\text{pH} = 7$; 3 – $\text{pH} = 9$; 4 – $\text{pH} = 11$

According to data presented in Table both Langmuir and Freundlich adsorption isotherm-models can be used to describe phenol adsorption onto glycopolymers. The evidence of this fact is close to 1 value of correlation coefficients R^2 . The maximum adsorption capacity of glycopo-

lymer (TDI) is higher than GP(HDI). TDI raises with increasing of polysaccharide hydroxyl groups substitution degree. In contrast to GP(TDI) the adsorption capacity of glycopolymer based on HDI decreases with increasing of polysaccharide hydroxyl groups substitution degree.

Relying on Freundlich equation calculated coefficients it can be concluded that the energy surface heterogeneity of GP(TDI) is higher than the heterogeneity of glycopolymer (HDI). That may indicate the presence various adsorption centres in GP(TDI) that hold the adsorbate molecules by different types of interactions. With increasing of hydroxyl groups substitution degree the energy surface heterogeneity of glycopolymer based on TDI increases.

It is known that phenol adsorption onto polysaccharide sorbents occurs by physical interaction between the adsorbent and adsorbate (hydrophobic interaction, hydrogen bonding and π - π interaction between aromatic rings) [11]. According to data obtained we can conclude that phenol molecules adsorption onto glycopolymer (HDI) occurs mainly through hydrophobic interaction and hydrogen bonding. Taking into account that glycopolymer (TDI) contains aromatic rings with π -conjugation which are absent in glycopolymer (HDI) the adsorption of phenols onto glycopolymer (TDI) can largely realize through π - π interaction between the aromatic rings of glycopolymer and phenols. The increasing of glycopolymer (TDI) energy surface heterogeneity with increasing of polysaccharide hydroxyl groups substitution degree as well as increasing of its maximum adsorption capacity confirm this supposition.

3.4. Effect of pH on Phenol Sorption onto Glycopolymers

The adsorption of phenol onto glycopolymer films is strongly influenced by solution pH.

In acidic medium (pH = 2) the adsorption equilibrium is reached in 2 h. In neutral or alkaline medium the adsorption equilibrium is achieved in 48 h. The isotherms obtained at pH 7 and 9 are very similar with higher adsorption capacity as compared with isotherms obtained at pH 2 and 11. The optimum adsorption of phenol achieved at pH = 7–9 is illustrated by Fig. 5.

It should be noted that phenol displays acid-base properties ($pK_a = 9.9$). When pH of the solution goes beyond 9.9 value, phenols exist mainly as negative phenolate ions. In the solution with pH below 9.9 phenols are molecules [12, 13].

The adsorption capacity of glycopolymers substantially increases in neutral and weakly alkaline mediums (where phenol remains in both molecular and ion forms). It can be supposed that phenols effectively adsorbed onto the adsorbent under such conditions are both molecules and phenolate anions. Such behavior can be related to the selective adsorption of different phenol forms onto GP active centres of different nature and power. In alkaline medium the adsorption occurs on one type of the centres and in acid medium – on another one. In neutral and weakly alkaline mediums we can observe

participation of all types of active centres in the absorption process.

Identification of glycopolymer active centres structure requires more detailed investigation.

4. Conclusions

New glycopolymers based on KGM cross-linked with water soluble blocked diisocyanates (TDI-ACA and HDI-ACA) were used for adsorption of phenol from aqueous solution. Adsorption behavior of GP depends on structure of diisocyanate and on polysaccharide group substitution degree.

Several parameters such as contact time, pH and initial phenol concentration were found to essentially affect the phenol removal efficiency. The optimum waste removal from the aqueous solution was achieved at pH = 7–9 with 24 h contact time and 0.05M initial phenol concentration. The data of the phenol adsorption by the glycopolymers were fitted by the Langmuir and Freundlich adsorption isotherm model, with correlation coefficients close to 1 for all GP. The adsorption capacities, as determined by the Langmuir isotherm model were 20.0; 25.0; 20.8 and 12.8 for GP(TDI)-40; GP(TDI)-80; GP(HDI)-40; and GP(HDI)-80, respectively.

Energy surface heterogeneity is higher for TDI-based glycopolymers as compared with HDI-based glycopolymers indicating the presence in GP(TDI) adsorption centres that hold the adsorbate molecules by different types of interactions.

References

- [1] Fan C., Sun Y., Min Y. *et al.*: Nonferrous Met. Soc. Chin., 2003, **13**, 1008.
- [2] Fazullin D., Mavrin G., Melkonyan R.: Chem. Tech. Fuels Oils, 2014, **50**, 53. <https://doi.org/10.1007/s10553-014-0493-5>
- [3] Al-Asheh S., Banat F., Abu-Aitah L.: Sep. Purif. Technol., 2003, **33**, 1. [https://doi.org/10.1016/S1383-5866\(02\)00180-6](https://doi.org/10.1016/S1383-5866(02)00180-6)
- [4] Wu C., Zhang J., Wang L. *et al.*: Water Sci. Technol., 2013, **67**, 1620. <https://doi.org/10.2166/wst.2013.038>
- [5] Valderrama C., Barios J., Farran A. *et al.*: Water Air Soil Pollut., 2011, **215**, 285. <https://doi.org/10.1007/s11270-010-0478-x>
- [6] Abussaud B., Asmaly H., Saleh A. *et al.*: J. Molec. Liq., 2016, **213**, 351. <https://doi.org/10.1016/j.molliq.2015.08.044>
- [7] Canizares P., Lobato J., Garcia-Gomez J. *et al.*: J. Appl. Electrochem., 2004, **34**, 111. <https://doi.org/10.1023/B:JACH.0000005607.37738.71>
- [8] Canizares P., Carmona M., Baraza O. *et al.*: J. Hazard. Mater., 2006, **131**, 243. <https://doi.org/10.1016/j.jhazmat.2005.09.037>
- [9] Crini G.: Prog. Polym. Sci., 2005, **30**, 38. <https://doi.org/10.1016/j.progpolymsci.2004.11.002>
- [10] Maistryshyn Ch.-N., Didenko K., Kozak N., Pobigai H.: Ukrainian-Polish scientific conference “Membrane And Sorption Processes And Technologies”, Ukraine, Kyiv 2015, 139.
- [11] Li J.-M., Meng X.-G., Hu C.-W. *et al.*: Bioresource Technol., 2009, **100**, 1168. <https://doi.org/10.1016/j.biortech.2008.09.015>

[12] Canizares P., Carmona M., Baraza O. et al.: J. Hazard. Mater., 2006, **131**, 243. <https://doi.org/10.1016/j.jhazmat.2005.09.037>

[13] Laszlo K., Tombacz E., Novak C.: Coll. Surf. A, 2007, **306**, 95. <https://doi.org/10.1016/j.colsurfa.2007.03.057>

Received: September 22, 2016 / Revised: October 28, 2016 /
Accepted: January 20, 2017

ОТРИМАННЯ СОРБЕНТІВ ФЕНОЛУ НА ОСНОВІ КОНЖАК ГЛЮКОМАНАНУ І ВОДОРОЗЧИННИХ БЛОКОВАНИХ ІЗОЦІАНАТІВ ТА ЇХ ХАРАКТЕРИСТИКА

Анотація. В роботі синтезовано та охарактеризовано водорозчинні блокovanі алкільні і арильні діізоціанати та

глікополімери на основі конжак глюкоманану і отриманих блокovanіх діізоціанатів. Проведено аналіз сорбційної здатності глікополімерів щодо фенолу. Адсорбцію було проведено для оцінки впливу структури ізоціанату, ступеня заміщення гідроксильних груп полісахариду, рН розчину, часу контакту на ефективність видалення фенолу. Для опису ізотерм адсорбції фенолу застосовано моделі Ленгмюра і Фрейндліха й оцінено параметри адсорбції. Значення адсорбційної ємності варіюється від 12,8 мг/г до 25,0 мг/г і залежить від структури ізоціанату і ступеню заміщення гідроксильних груп полісахариду. Було показано сприятливий вплив нейтрального і слаболужного середовища на адсорбцію фенолу на глікополімерах.

Ключові слова: блокovanі діізоціанати, полісахарид, конжак глюкоманан, адсорбція фенолу, ізотерма адсорбції.