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INVESTIGATION OF SORPTION PROPERTIES OF A DISPERSED SYSTEM OBTAINED FROM NATURAL BIOPOLYMERS

Abstract. In this paper, the regularities of the processes of structure formation of mixed aqueous solutions of sodium humate with a natural polymer – gelatin are studied and their sorption properties are studied. The choice of gelatin as a natural polymer is due to its high gel-forming properties, the presence of functional groups that contribute to the formation of intermolecular bonds, as well as industrial availability.

To obtain a dispersed system, a method of mixing water solutions of the initial components is used, in which the self-organizing forces of the initial polymer components are manifested. The modifying influence of humate, pH of the medium and time on the process of system structure formation is studied. It is assumed that the stability of mixtures is related to the structure of the structure of humate and gelatin. That when combined, various forces of intermacromolecular interaction come to the fore and self-organizing capabilities of polymers are realized, which lead to a significant improvement in the properties of the original polymers. It is noted that the directed modification by combining polymers gives almost limitless possibilities for their application in various fields, primarily in wastewater treatment. Sorption properties of absorption of copper, nickel and lead ions from aqueous solutions of their salts were studied for the obtained mixtures of different compositions. The influence of the ratio of initial components on sorption is estimated. It was found that the sorption activity of polymer-polymer complexes increases with the increase in the humate mixture. The effectiveness of their application in sorption processes is shown and they are recommended as sorbents for wastewater treatment from heavy metal ions.

Key words: dispersion system, gelatin, sodium humate, sorption, sorbent, cleaning.

Introduction. Polymer materials are increasingly used in various fields of industry and in everyday life due to the ability to regulate the composition and an unlimited variety of properties.

Recently, researchers of various profiles have been paying close attention to the issues of obtaining a dispersed system from natural high-molecular compounds and studying their sorption properties [1-3].

One of the most important methods for obtaining such dispersion systems is mixing various polymer solutions. When combined, various forces of intermacromolecular interaction come to the fore and self-organizing capabilities of polymers are realized, which lead to a significant improvement in the properties of the original polymers. Directed modification by combining polymers gives almost limitless

possibilities for using polymer-polymer complexes in different fields. Polymer-polymer complexes are a new class of composite materials that can exhibit higher sorption properties, hydrolytic stability, and strength in comparison with the original components. The method of obtaining them is the most economical and technological method and allows in many cases to fundamentally change the performance properties of materials, reduce their cost [4-7].

Natural polymers offer great prospects for obtaining practically significant and environmentally safe polymer-polymer complexes. The most widely used biopolymer is gelatin.

Gelatin is the most widely studied and natural gel-forming, highly symmetric polypeptide polymer of protein nature, in which individual parts of macrocycles bind a peptide bond with NH–CO. It consists of 5 α-amino acids (the predominant γ-glycine), it is a typical polyampholite. The presence of peptide bonds, acidic and basic groups determines the ability of gelatin to form donor-acceptor complexes with humic acids. The isoelectric point of gelatin is located in the pH range from 4.8 to 5.1 [8, 9].

Natural ion-containing polymers include humic acids, which are formed in nature as a result of biochemical transformations of land vegetation and make up the main part of the organic mass of coal, peat and soil.

Humic acids (HA) are characterized by the presence of a condensed aromatic core and an exceptionally rich functional composition. They exhibit properties of colloidal substances, have surface-active properties, and participate in donor-acceptor and sorption interactions.

Numerous studies have shown that humic acids can bind almost all types of ecotoxicants, including transition metal ions and radionuclides [10].

Due to the lack of systematic research in the field of obtaining and using polymer-polymer complexes based on humic acid with natural polymer – gelatin, and taking into account the high complexing potential of humic acids, it seemed relevant to conduct research in this area.

The main purpose of this work is to study the dispersion system obtained from natural biopolymers and study their sorption properties [11].

EXPERIMENTAL PART

The initial raw material for obtaining humic acid was oxidized coals of the Shubarkol Deposit with a humic acid content of up to 60-80%. The work used a salt form of humic acid, in the form of sodium humate, which was isolated by alkaline extraction from oxidized coals of the Shubarkol Deposit. Feature SH: ∑COOH+OH is 4.5 mg-eq/g, ∑COOH – 3,0-3,5 mg-eq/g, A – 13-15 %, W^a – 10-12%, a nitrogen content of less than 1% [12-14].

Gelatin was used as a natural polymer. Gelatin solutions were prepared as follows: a certain amount of water was added to the gelatin suspension and left to swell for 10-12 hours at 10^0C. Then the flask with the swollen gelatin after adding the necessary amount of water was immersed in a water bath, heated to 50^0C and

kept in it until the gelatin completely dissolved. Characteristics of gelatin: humidity - 15%, ash content - 2 %, molecular weight – 70 000, d^{20} - = 1368 kg/m^3 [15].

The viscosity of polymer-polymer complexes was determined using a Ubellode viscometer with a capillary diameter d = 0,56 at 293 K with an accuracy of ± 0,5^{o}C.

To obtain polymer-polymer complexes based on sodium humate with gelatin, the method of mixing aqueous solutions of the initial components in various volume ratios at room temperature was used. Polymer-polymer complexes are stable in aqueous solution and there is no delamination. When dried, black films are formed.

To determine the sorption capacity of polymer-polymer complexes of different compositions, the absorption of Cu (II), Ni (II) and Pb (II) ions from aqueous solutions of their salts at a concentration of 0.025 mol/l after a day was studied. When the sorption equilibrium is reached in the solution, the equilibrium concentration of metal ions is determined by complexometric titration. The sorption capacity of the rock was estimated by the static exchange capacity of SEC, mg-eq/g [16,17].

RESULTS AND DISCUSSION

The results of the study showed that when mixing aqueous solutions, where the main component is a natural polymer-gelatin, and sodium humate is a modifier, homogeneous mixtures are formed that do not delaminate over time. The content of the modifier varied from 2 to 10 wt.% relative to the main polymer. The gelatin concentration was 7%. The choice of this concentration is due to the achievement of a critical concentration of gelation, which forms jellies with practically measurable strength. Their resistance to delamination is due to the action of intermolecular forces and the formation of hydrogen bonds between the original macromolecules [18].

The study of structure formation processes was carried out by changing the relative viscosity for mixtures of different compositions in time and pH. The relative viscosity of mixed solutions was determined by the viscometric method in thermostatically controlled capillary viscometers. The kinetics of structure formation processes in mixed solutions of gelatin with sodium humate is shown in table 1.

Table 1 shows that the highest relative viscosity values for gelatin mixtures with humate are observed at pH 3.The minimum viscosity is observed near the isoelectric point at pH 5, when all positive and negative charges are compensated and favorable conditions are created for compacting the macromolecules of the mixture. With an increase in the humate content in the mixture, the gelation time increases.

Obtaining stable, homogeneous, non-delaminating mixtures over time is associated with the structure of the structure of humate and gelatin. Such reactions are described by the basic laws established for the reaction between oppositely charged polyelectrolytes, since both humate and gelatin exhibit typical polyelectrolyte properties in aqueous solutions. Gelatin as a microporous substance has a very developed surface, so that in contact with an aqueous solution, both solvent and sodium humate penetrate into its array [19, 20].

Table 1 – Kinetics of changes in the relative viscosity of aqueous solutions of gelling polymer depending on the content of sodium humate and the holding time at 20°C

№	Time, day	Relative viscosity, η_{rv}, at the content of sodium humate in the mixture (%wt.)					
		0	2	4	6	8	10
Gelatin-sodium humate, pH 3							
1	0	1,50	1,45	1,41	1,37	1,33	1,28
	1	1,56	1,52	1,48	1,44	1,40	1,37
	2	1,60	1,56	1,52	1,48	1,44	1,41
	3	1,62	1,58	1,54	1,50	1,47	1,43
	4	1,66	1,63	1,60	1,58	1,55	1,53
Gelatin-sodium humate, pH 5							
2	0	1,24	1,21	1,19	1,16	1,13	1,12
	1	1,34	1,31	1,30	1,29	1,26	1,22
	2	1,40	1,37	1,34	1,31	1,28	1,26
	3	1,4	1,43	1,40	1,37	1,34	1,32
	4	1,54	1,51	1,48	1,45	1,43	1,40
Gelatin-sodium humate, pH 9							
3	0	1,30	1,28	1,25	1,23	1,21	1,19
	1	1,37	1,35	1,33	1,30	1,28	1,26
	2	1,42	1,40	1,37'	1,35	1,32	1,30
	3	1,46	1,44	1,41	1,39	1,37	1,35
	4	1,53	1,50	1,48	1,45	1,43	1,40

Despite the complexity of studying the sorption mechanism, the resulting polymer-polymer complexes can be considered as effective absorbers of both cations and anions due to their structural organization.

Sorption properties were studied for the obtained polymer-polymer complexes of different compositions. To determine the sorption capacity of polymer gelatin-humate films of different compositions, the absorption of Cu (II), Ni (II) and Pb (II) ions from aqueous solutions of their salts with a concentration of 0.025 mol/l after a day was studied. When the sorption equilibrium is reached in the solution, the equilibrium concentration of metal ions is determined by complexometric titration with a solution of Trilon B. The sorption capacity of polycomplexes was estimated by the static exchange capacity of SEC. The results of the study of sorption of metal ions by the obtained complexes are shown in table 2.

Table 2 – Sorption of metal ions on gelatin-humate complexes of different composition

Gelatin : humate, the amount. %	SEC, mg-eq/g					
	Cu^{2+}		Ni^{2+}		Pb^{2+}	
	exper.	theoret.	exper.	theoret.	exper.	theoret.
100:0	0,13	0,13	0,38	0,38	1,00	1,00
90:10	0,38	0,36	0,75	0,54	1,25	1,14
60:40	1,00	1,03	1,00	1,02	1,50	1,55
50:50	1,25	1,26	1,13	1,19	1,63	1,69
40:60	1,75	1,48	1,38	2,10	1,88	1,82
10:90	2,25	2,15	1,75	1,35	2,13	2,23
0:100	2,38	2,38	2,00	2,00	2,37	2,37
*The salt concentration of 0.025 mol/l, S:L = 1:250, 20°C, 1 day.						

The data in table 2 allow us to evaluate the effect on sorption of the composition of the complex with a different ratio of gelatin and humate, the nature of the metal ion, and also to compare the sorption capacity of humate. Table 2 shows that polymer-polymer complexes have sufficient sorption capacity in relation to metal ions of copper, nickel and lead. As the humate mixture increases, the sorption activity of polycomplexes increases and is 0.38-2.25 mg-eq/g, depending on the composition. The obtained SEC values are comparable to the calculated values. A small synergistic increase is observed in the sorption of copper ions. A synergistic increase in the complexing ability of nickel in a gelatin medium was also found. SEC sorbents for nickel in the absence of gelatin do not exceed the value of 2.0 mg-eq/g. Lead ions in a mixed gelatin gel slightly reduce their complexing activity and, on average, show lower values of SEC than copper and nickel ions. The resulting polymer-polymer complexes can be recommended as sorbents in water treatment processes from heavy metal ions.

Conclusion. Thus, the research shows that polymer-polymer complexes based on humate and gelatin are obtained by a simple method of mixing their aqueous solutions. The regularities of the processes of their structure formation are studied using viscometry methods. The determining role of the concentration of the modifying additive, as well as the pH of the medium on the process of structure formation of the system is shown. Sorption properties of the obtained polymer-polymer complexes are investigated. The effectiveness of their application in sorption processes as sorbents for wastewater treatment from heavy metal ions is shown.

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Резюме

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ТАБИҒИ БИОПОЛИМЕРЛЕРДЕН АЛЫНҒАН ДИСПЕРСТІ ЖҮЙЕНІҢ СОРБЦИЯЛЫҚ ҚАСИЕТТЕРІН ЗЕРТТЕУ

Жұмыста табиғи полимерлі – желатині бар натрий гуматының аралас су ерітінділерінің құрылым түзілу процестерінің заңдылықтары зерттелген және олардың сорбциялық қасиеттері зерттелген. Желатинді табиғи полимер ретінде таңдау – оның жоғары гель түзетін қасиеттеріне, функционалдық топтардың құрамындағы молекулааралық байланыстардың пайда болуына ықпал етуіне, сондай-ақ өнеркәсіптік қол жетімділігіне негізделген.

Дисперсиялық жүйені алу үшін бастапқы компоненттердің су ерітінділерін араластыру әдісі қолданылады, онда бастапқы полимерлік компоненттердің өздігінен ұйымдастырылатын күштері көрінеді. Гуматтың, pH ортаның және уақыттың жүйенің құрылым құру процесіне түрлендіруші әсері зерттелді. Қоспалардың тұрақтылығы гумат пен желатин құрылымының ерекшеліктерімен байланысты. Бірінші жоспарға біріктірілген кезде полимераралық өзара әрекеттесудің әр түрлі күштері шығады және бастапқы полимерлердің қасиеттерін айтарлықтай жақсартуға әкелетін полимерлердің өзін-өзі ұйымдастыру мүмкіндіктері іске асырылады. Полимерлерді біріктіру жолымен бағытталған модификация оларды әртүрлі салаларда және бірінші кезекте ағынды суларды тазалауда қолдануға шексіз мүмкіндік беретіні атап өтілді. Әртүрлі құрамдағы алынған қоспалар үшін олардың тұздарының су ерітінділерінен мыс, никель және қорғасынның иондарын сіңіру бойынша сорбциялық қасиеттері зерттелді. Бастапқы компоненттердің арақатынасы сорбцияға әсері бар екендігі бағаланды. Гумат қоспасының өсуімен полимер-полимерлі кешендердің сорбциялық белсенділігі өседі. Сорбциялық процестерде оларды қолданудың тиімділігі көрсетілген және ағынды суларды ауыр металл иондарынан тазарту үшін сорбент ретінде ұсынылған.

Түйін сөздер: дисперсиялық жүйе, желатин, натрий гуматы, сорбция, сорбент, тазалау.

Резюме

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ИССЛЕДОВАНИЕ СОРБЦИОННЫХ СВОЙСТВ ДИСПЕРСНОЙ СИСТЕМЫ, ПОЛУЧЕННОЙ ИЗ ПРИРОДНЫХ БИОПОЛИМЕРОВ

В работе изучены закономерности процессов структурообразования смешанных водных растворов гумата натрия с природным полимером – желатином и изучены их сорбционные свойства. Выбор желатина в качестве природного полимера обусловлен его высокими гелеобразующими свойствами, наличием в составе функциональных

групп, способствующих образованию межмолекулярных связей, а также промышленной доступностью.

Для получения дисперсной системы использован метод смешения водных растворов исходных компонентов, при котором проявляются самоорганизующие силы исходных полимерных компонентов. Изучено модифицирующее влияние гумата, pH среды и времени на процесс структурообразования системы. Предположено, что стабильность смесей связано с особенностями строения структуры гумата и желатина. Что при совмещении на первый план вступают различные силы межмакромолекулярного взаимодействия и реализуются самоорганизующие возможности полимеров, которые приводят к значительному улучшению свойств исходных полимеров. Отмечено, что направленная модификация путем совмещения полимеров дает практически безграничные возможности их применения в разных областях и в первую очередь в очистке сточных вод. Для полученных смесей разного состава изучены сорбционные свойства по поглощению ионов меди, никеля и свинца из водных растворов их солей. Оценено влияние на сорбцию соотношение исходных компонентов. Установлено, что с возрастанием в смеси гумата сорбционная активность полимер-полимерных комплексов возрастает. Показана эффективность их применения в сорбционных процессах и рекомендованы в качестве сорбентов для очистки сточных вод от ионов тяжелых металлов.

Ключевые слова: дисперсионная система, желатин, гумат натрия, сорбция, сорбент, очистка.