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POLYCOMPLEXES BASED ON BIOPOLYMERS

Abstract. Studies of polymer complexes of humic acids with a synthetic polymer have broad prospects for directed modification of humic acids and for the creation of a new class of composite materials of various applications. As part of the creation of effective and environmentally friendly technologies for deep processing of coal mining waste and the production of new valuable import-substituting chemical products for multi-purpose purposes, studies have been conducted to obtain self-organizing humic polymers and their complexes with a synthetic polymer. The raw material for the production of sodium humate was oxidized coals of the Shubarkol Deposit with a content of humic acids up to 60-80%, isolated by alkaline extraction. As a synthetic polymer, polyacrylamide with a high molecular weight of $5.0 \cdot 10^5$, with a degree of hydrolysis of 10%, a content of carboxyl groups – 1.4 mg-eq/g and a characteristic viscosity – 6.2 was used. By the method of mixing solutions, polymer complexes of sodium humate with polyacrylamide were obtained and characterized. Their acid and sorption properties by copper ions were studied. The analysis of metal ions was carried out by the complexometric method. Synergetic effects of increasing acidic and sorption properties for the obtained polymer complexes were revealed, which manifest themselves about 30-40%. The application areas determined for obtained polycomplexes.

Keywords: polycomplexes, sodium humate, humic acids, polymers, polyacrylamide, sorption, complexometric method.

Introduction. The processes of structure formation between polymers with heterogeneous macromolecules are widespread in nature and are carried out in various industries. To date, there have been quite a large number of publications devoted to the problem of obtaining and applying polymer complexes by combining, which indicates their importance for a number of production processes, as well as for modeling complex biochemical processes [1-4]. Directed modification by combining polymers gives almost limitless possibilities for the use of polymer complexes in various fields of technology for the production of polymer coatings, films, binders, catalysis, medicine, bioengineering, textile and paper industries, processes of extraction, separation and concentration of metal ions and organic substances, as well as in other fields of science and technology [5].

Natural polymers present great prospects for obtaining practically significant and environmentally safe polymer gels and complexes. Natural ion-containing polymers include humic acids, formed in nature as a result of biochemical transformations of terrestrial vegetation and constituting the bulk of the organic mass of coal, peat, soils and sapropels.

Currently, there are various mixtures of humic acids, which are used in medicine, animal husbandry, poultry. Due to the lack of systematic research in the field of production and application of polymer complexes of humic acids with synthetic polymers and given the high natural complexing potential of humic acids, it seemed relevant to conduct research in this area. The combination of waste products with synthetic polymers leads to the creation of a new composite material, the properties of which are quantitatively and qualitatively different from the properties of each of its components. Varying the composition of the composite material, you can get a wide range of materials with the desired set of properties. Therefore, many composite materials are superior to traditional materials in their mechanical properties.

The aim of the work is to obtain polycomplexes based on sodium humate with polyacrylamide, and study their sorption properties [6-8].

EXPERIMENTAL PART

Oxidized coals of the Shubarkol Deposit contain humic acids about 60-80%, and is the initial raw material for the production of humic acids. In this work a salt form of humic acid such as sodium HUMATE, isolated by alkaline extraction from oxidized coals was used. HPa characteristic: ∑COOH+OH – 4.5 mg-eq/g, ∑COOH – 3,0-3,5 mg-eq/g, A- 13-15%, W^a – 10-12%, nitrogen content-less than 1%.

A synthetic polymer - polyacrylamide (PAA) has following characteristics: molecular weight about $5.0 \cdot 10^5$ a.u.m. , a degree of hydrolysis of 10%, content of carboxyl groups – 1.4 mg-eq/g, and a characteristic viscosity of - 6.2. PAA is practically insoluble in organic solvents, and its melting point is 113°C. At interacting with water, polyacrylamide forms a gel. The average pH level can vary in the range of 7-14. The analysis of metal ions was carried out by the complexometric method.

To obtain polycomplexes of sodium humate with polyacrylamide, the 0.5% aqueous solutions of the initial components in various volume ratios were mixed at room temperature. Aqueous solutions of polymer complexes are stable, and delamination is not observed. At drying dark brown powders formed [9-13].

RESULTS AND DISCUSSION

Studies of polymer complexes of humic acids with various synthetic polymers have broad prospects for directed modification of humic acids and for the creation of a new class of composite materials of various applications, which can exhibit higher sorption properties, hydrolytic stability, strength and other specified properties in comparison with the initial compounds [14]. Humic acids are characterized by the presence of a condensed aromatic nucleus and an exceptionally rich functional composition. They exhibit the properties of colloidal substances, have surface-active properties and belong to self-organizing anionic polyfunctional

polyelectrolytes. The polyfunctionality of humic acids determines their ability to enter into ion exchange reactions, electron transfer (redox reactions) and complexation.

One of the little-studied ways to increase the desired humic acids and new practically important characteristics is the creation on their basis of polymer complexes with synthetic polymers [15].

The synthetic polymer used in the work, polyacrylamide, $(C_3H_5NO)_n$, is a universal chemical substance. The widespread use of PAA is due to its special chemical properties. PAA finds its application in various fields of human activity: in the oil refining industry, in medicine, in molecular biology, in the mining and processing sector. It is used in the production of polymer packaging, as well as as flocculants in the wastewater treatment process.

By mixing 0.5% aqueous solutions of the initial components in different volume ratios, at room temperature, we obtained polycomplexes of sodium humate with polyacrylamide of different composition [16]. The influence of the initial mixture composition on the process of structure formation is investigated. Noted that the determining factors of the process of formation of selected compounds and complexes are polymerchemistry concentration of the compound and pH, which is associated with the need to achieve a critical concentration of structuring. The conductometric method was used to study the acid-base composition and evidence of the formation of polycomplexes. The experimental data on the content of acid groups in PAA-GNa polycomplexes in comparison with additive values are presented in table 1.

Table 1 – Acidic properties of GN a-PAA polycomplexes of different composition

Composition of initial mixture G Na: PAA		∑COOH+OH, Mg-EQ/g	
mass ratios,%	molar ratios.%	exp.	addit.
0 : 100	0 : 100	3,10	3,10
10 : 90	40 : 60	3,40	3,29
20 : 80	60 : 40	3,60	3,48
30 : 70	70 : 30	3,90	3,67
40 : 60	80 : 20	4,50	3,86
50 : 50	85 : 15	4,15	4,05
60 : 40	90 : 10	3,50	4,24
70 : 30	93 : 7	3,20	4,43
80 : 20	96 : 4	3,33	4,62
90 : 10	98 : 2	3,33	4,80
100 :0	100 :0	5,00	5,00

It is known that polyacrylamide is used as a flocculant in wastewater clarification, coagulant in metallurgy, flotation agent, dispersant, thickener. In water, polyacrylamide is gradually hydrolyzed to the ammonium salt of polyacrylic acid. Its macromolecules contain oxygen and nitrogen atoms, which act as proton acceptors. Amide and carboxylate groups of multicolored PAA participate in the formation of complexes [17].

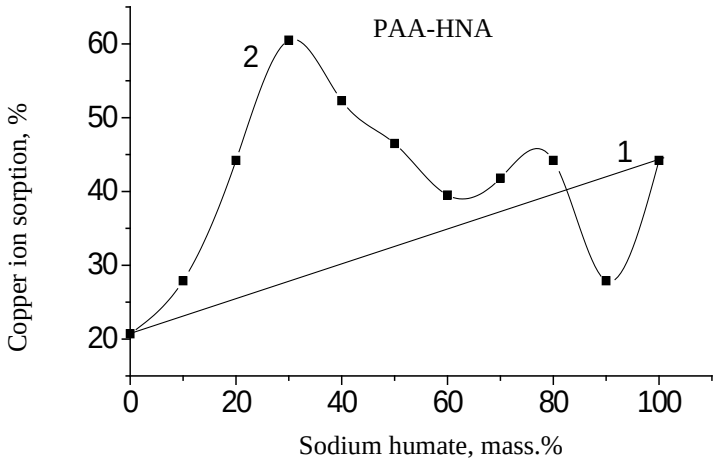
As can be seen from data table 1 with a higher content of humate in the mixture (50-90%) the complexation of humate with PAA occurs as a result due to the formation of hydrogen bonds between the acid and amide groups of initial components. At the content of humate in the mixture less than 40 mass %, a synergistic effect of acid groups is manifested.

Using the obtained polycomplexes of humate with polyacrylamide their sorption properties for copper ions were studied. The obtained experimental data and calculated additive ESR values were compared (table 2, figure).

The data of table 2 and the curve of the dependence on the sorption of copper ions by PAA polycomplexes - sodium humate on the composition of the initial mixture (figure) have two maxima: high - in the region of 80 mass.%, and insignificant in the region of 45% humate content in the mixture. In the area of 35-45% humate in the complex there is a synergistic effect of increasing the sorption of copper ions [18-20].

Table 2 – Sorption properties of HNA-PAA polycomplexes of different composition by copper ions ([Cu2+] - 0.025 mol/l)

Composition of the initial mixture NaH:PAA		SOE (Cu^{2+}), mg-eq/g		Sorption, %
mass ratios.%	molar ratios.%	exp..	addit.	exp..
0 : 100	0 : 100	1,19	1,19	20,7
10 : 90	40 : 60	1,84	1,31	27,9
20 : 80	60 : 40	1,45	1,43	44,2
30 : 70	70 : 30	1,80	1,54	60,5
40 : 60	80 : 20	1,65	1,66	52,3
50 : 50	85 : 15	1,52	1,79	46,5
60 : 40	90 : 10	1,48	1,91	39,5
70 : 30	93 : 7	1,53	2,03	41,8
80 : 20	96 : 4	1,75	2,14	44,2
90 : 10	98 : 2	1,68	2,26	27,9
100 :0	100 :0	2,38	2,38	44,2



Dependence on of copper ion sorption by HNA – PAA polycomplex:
1 - additive curve, 2 - experimental curve

Conclusion. Thus, based on experimental data have shown that polymer complexes of sodium humate with a synthetic polymer were formed by mixing their aqueous solitions. Acidic and sorption properties of polymer complexes have been studied using copper ion. Synergistic effects of increasing acid and sorption properties for polymer complexes have been found.

The obtained polycomplexes can be recommended as sorbents for purification wastewater treatment from heavy metals.

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Резюме

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БИОПОЛИМЕР НЕГІЗІНДЕГІ ПОЛИКОМПЛЕКСТЕР

Синтетикалық полимерлі гумин қышқылдарының полимерлі кешендерін зерттеу, гумин қышқылдарының бағытталған модификациясы мен кең ауқымды қолданбалы композициялық материалдардың жаңа класын құрудың кең перспективаларына ие. Көмір қалдықтарын терең өңдеудің тиімді және экологиялық таза технологияларын құрудың кең ауқымды мақсатта пайдалану үшін, жаңа құнды импортты алмастыратын химиялық өнімдерді өндіру аясында синтетикалық полимерлермен өзін-өзі ұйымдастыратын гуминді полимерлер мен олардың комплекстерін алу бойынша зерттеулер жүргізілді. Натрий гуматын өндіруге арналған бастапқы шикізат ретінде Шұбаркөл кен орнының тотыққан көмірлерінен сілтілік экстракциямен 60-80% дейін сірінділенген гумин қышқылдары болып табылады. Синтетикалық полимер ретінде молекулалық салмағы $5{,}0 \cdot 10^5$ м.а.б. болатын , гидролиз деңгейі 10%, карбоксил тобының мөлшері 1,4 мг-экв/г және сипаттауыш тұтқырлығы 6,2 болатын полиакриламидтер пайдаланылды. Натрий гуматының полиакриламидпен полимерлі кешенді қосылыстары олардың ерітінділерін араластыру арқылы алынды. Олардың қышқылдық және сорбциялық қасиеттері мыс иондары қатысында зерттелінді. Металл иондарын анықтау комплекстометриялық әдіспен жүргізілді. Алынған

полимерлі кешендер үшін натрий гуматының 30-40% мөлшерінде олардың қышқылдық және сорбциялық қасиеттердің жоғарылауының синергетикалық әсерлері анықталды. Алынған поликомплекстер, шайынды су құрамын ауыр металл иондарынан тазартуда қолданылады.

Түйін сөздер: поликомплекстер, натрий гуматы, гумин қышқылдары, полимерлер, полиакриламид, сорбция, комплексометрия.

Резюме

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ПОЛИКОМПЛЕКСЫ НА ОСНОВЕ БИОПОЛИМЕРА

Исследования полимерных комплексов гуминовых кислот с синтетическим полимером имеют широкие перспективы для направленной модификации гуминовых кислот и для создания нового класса композиционных материалов самого разнообразного применения. В рамках создания эффективных и экологически безопасных технологий по глубокой переработке отходов угледобычи и производству новой ценной импортозамещающей химической продукции многоцелевого назначения проведены исследования по получению самоорганизующихся гуминовых полимеров и их комплексов с синтетическим полимером. Исходным сырьем для получения гумата натрия служили окисленные угли Шубаркольского месторождения с содержанием гуминовых кислот до 60-80%, выделенный методом щелочной экстракции. В качестве синтетического полимера использован полиакриламид с высокой молекулярной массой $5{,}0 \cdot 10^5$ а.е.м., со степенью гидролизованности 10%, содержанием карбоксильных групп – 1,4 мг-экв/г и характеристической вязкостью – 6,2. Методом смешения растворов получены и охарактеризованы полимерные комплексы гумата натрия с полиакриламидом. Изучены их кислотные и сорбционные свойства по ионам меди. Анализ ионов металлов проводили комплексонометрическим методом. Обнаружены синергетические эффекты повышения кислотных и сорбционных свойств для полученных полимерных комплексов, проявляющиеся при содержании исходных гуматов натрия 30-40%. Определены области применения полученных поликомплексов.в очистке сточных вод от ионов тяжелых металлов.

Ключевые слова: полимкомплекс, гумат натрия, гуминовые кислоты, полимеры, полиакриламид, сорбция, комплексометрический метод.