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INTERACTION OF Cr (III) IONS WITH SODIUM HUMATE IN ACQUEOUS MEDIUM

Abstract. The regularities of the influence of chromium ions concentration and sodium humate rate on the process of complex formation upon the interaction of chromium (III) chloride with sodium humate have been studied. In the course of the performed works it has been established that an increase in the concentration of the chromium ions rate from 0,005 up to 0,5% and the sodium humate rate from 0,1 up to 1,0 g contributes to increasing of the yield of humic substances up to 36,49% and chromium mass content up to 4,31%. Shifting of pH to the acidic field and the IRS data, have shown the formation of humate complex compounds with chromium ions. IR-spectra of the studied samples of complex humic compounds show complexity of their composition. It follows from the data of thermal analysis of the obtained complex compounds that the introduction of chromium ions into the structure of humic compounds in the form of Me-O bond contributes to the acceleration of the processes of oxidation of humic compounds (the organic part) until complete burning-out of humates at the temperature up to 550°C. At the temperatures above 940°C the processes of destruction of the mineral part of humates start. The results of the functional analysis testify to the interaction of sodium humate with chromium ions, though no complete substitution of carboxylic and phenolic groups for chromium ions occurs. It has been established that other functional groups of humic compounds participate in the reactions of complex formation.

Keywords: sodium humate, chromium chloride, complex formation, functional groups.

Introduction. Due to a specific combination of different functional groups and paramagnetic centers humic compounds enter into the ionic and donor-acceptor interactions, participate in oxidation-reduction and sorption processes [1-4]. An ability of humic compounds to ion exchange and complex formation provides for the possibilities of their usage for water purification from heavy metals. The formation of complexes with humic substances results in lowering of their free form concentration and decreasing of toxicity. That is why humic compounds are applied as natural detoxicants, and a chemical modification of humates increases their sorption properties. Herewith, humic compounds are complex polyfunctional ligands, requiring a special approach upon the study of their complex-forming properties. In this connection, a study of complex-forming properties of the modified humic compounds with chromium ions is rather topical.

The goal of the study is an investigation of the regularities of the interaction process of sodium humate with chromium ions, a study of the dependence of the composition and properties of the new complex compounds upon different factors.

EXPERIMENT

Chemicals and instrumentation. Sodium humate of the following composition, mass %, was used in this work: yield of free humic acids (HA^{daf}) – 41,02; ash content (A^a) – 21,40; humidity (W^a) – 12,97, and chromium chloride (III). The experiments were carried out at 60°C and the process duration was 60 min with constant stirring of the reaction mixture.

Infra-red spectra of the studied samples were registered in tablets with KBr on IR-Furrier spectrometer Nicolet 5700, “Thermo Electron” (USA) in the field of 200-4000 cm^{-1} . Assignment of the absorption bands in IR-spectra was carried out in accordance with the literature data [5, 6]. Thermal gravitational analyses were carried out on derivatograph Q-1000/D of the F.Paulik, J.Paulik and L.Erdey system, manufactured by “MOM” company (Budapest). Shooting was carried out in the air medium in the temperature range of 20 - 1000°C. Heating regime was linear ($dT/dt = 10$ degree/min), a reference substance was incinerated Al_2O_3 , sample weight was 300 mg. Sensitivity of the measuring systems of the device was set up to be equal for the samples: TG = 100 mg = 500 μV , DTA = 250 μV , DTG = 500 μV , T = 500 μV . The analysis results were compared with the data, provided in the atlases of thermal curves [7, 8] and with the description of the destruction of monomineral samples, provided in reference sources and in the database. The microstructure of the samples was studied on electron probe micro-analyzer “JXA-8230”, produced by “JEOL” company (Japan) with accelerating voltage of 25 kV and electron stream current up to 100 nA. A spot energy-dispersion spectroscopic (EMF) analysis, EMF-mapping of the site by elements, EMF-microanalysis of the chosen site and semi-quantitative wave-dispersion spectroscopic analyses were made. For each analysis an adjustment by carbon was carried out, the signal of which was registered due to the applied two-sided carbonic conducting tape, on which the samples were mounted [9, 10]. The content of chromium was determined by an atomic-absorption method with the use of atomic-absorption spectrometer AA240, manufactured by “Varian Optical Spectroscopy Instruments” (Australia). The yield of free humic acids was determined according to [11], the content of the functional groups – following the methods [5].

Results and discussion

The present paper has studied the influence of the concentrations of chromium ions and the sodium humate rate upon the composition and properties of the obtained compounds. The experimental data have shown that increasing of the concentrations of chromium ions from 0,005 up to 0,5% leads to an increase in the yield of humic substances and chromium mass fraction (figure 1). Thus, with chromium chloride concentration of 0,005%, the yield of humic substances makes up 13,60%, chromium mass fraction – 0,14%, and with the concentration of 0,5% it increases correspondingly up to 36,49% and 4,31%. Probably, upon the

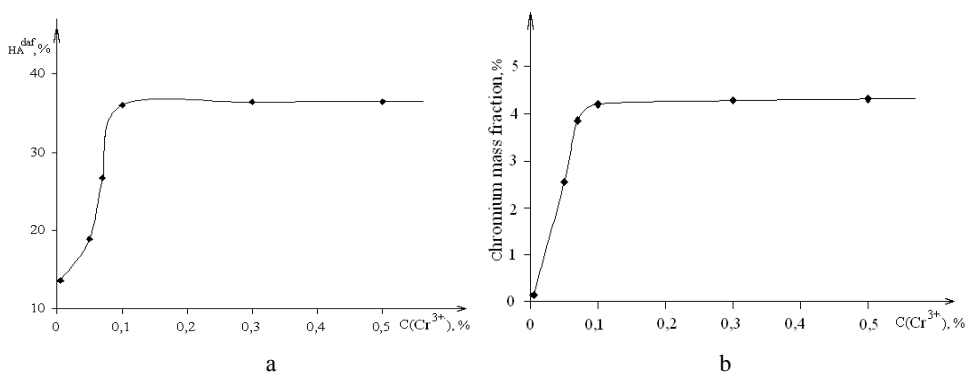


Figure 1 – An isotherm of the dependence of the yield of humic acids (a) and chromium mass fraction (б) upon the concentration of chromium ions

interaction of sodium humate with chromium ions an ion exchange reaction proceeds due to hydrogen of carboxylic groups and phenolic hydroxyls, with which insoluble chromium humates are formed, as well as the reactions, leading to the formation of complex compounds.

It is known that pH shifting to the acidic field is characteristic for the complex formation process. As it is seen from table 1, with an increase of the concentrations of chromium ions a decrease of pH from 9,17 down to 4,65 is observed. The presence of a large number of functional groups in humic compounds, as well as pH shifting to the acidic field upon the formation of precipitates, allows one to assume a formation of complex compounds of chromium ions with sodium humate.

Table 1 – Change of pH in dependence of the concentrations of chromium ions

Concentration of chromium ions, %					
0,005	0,05	0,07	0,1	0,3	0,5
9,17	8,25	7,59	6,45	4,90	4,65

In the obtained samples the contents of carboxylic and phenolic hydroxylic groups are determined (table 2). As it is seen from table 2, the studied samples differ considerably by the content of acidic functional groups. It has been established that with an increase of the concentrations of chromium ions from 0,005 up to 0,5% the number of chromium-substituted carboxylic groups increases, and the content of phenolic groups, bound with chromium, decreases. For example, upon the interaction of sodium humate with chromium chloride a number of carboxylic groups, bound with chromium, increases from 0,35 to 0,45 mg-equ per 100 g of the organic mass. An increase in the concentrations of chromium ions results in a decrease of the content of phenolic groups, substituted for chromium, from 1,65 up down to 1,50 mg-equ/g. A decrease of pH confirms the obtained results. This testifies to the fact that in the reactions of complex formation with chromium ions

Table 2 – Influence of the concentration of chromium ions upon the content of the functional groups in the obtained samples

C(Cr ³⁺), %	Content of acidic groups, mg-equ/g		
	COOH	OH _{phen.}	COOH+ OH _{phen.}
0,005	0,35	1,65	2,00
0,05	0,37	1,62	1,99
0,07	0,38	1,61	1,99
0,1	0,39	1,60	1,99
0,3	0,43	1,53	1,96
0,5	0,45	1,50	1,95

mainly carboxylic groups take part. However, no complete substitution of carboxylic groups by chromium ions has been observed under conditions of the conducted experiments.

It follows from the analysis of the IRS results (figure2), that a poly-component structure and complexity of the composition of the studied samples produce an effect upon the character of the spectra, a mutual influence of some absorption bands is observed to the extent of their merging, broadening and shifting, etc. It is noteworthy that in case of appearance of a new phase in the composition of the obtained products the values of the absorption band of this compound in the spectrum of the studied samples should not obligatory coincide with the value of the same band in the spectrum of the same individual compound, in view of the presence of other substances, making the general picture of the spectrum more complex. For example, the IR-spectra of the studied samples contain a large number of absorption bands, characteristic for different functional groups of humic compounds [5, 6]. In the spectra of the obtained products intensive absorption bands of valence vibrations of hydroxylic groups, forming intermolecular hydrogen bonds, are observed in the fields of 3550-3545, 3480-3475 and 3415-3410 cm⁻¹, the weak bands at 3290-3285 cm⁻¹ belong to valence vibrations of OH-groups in the complex compounds, the intensity of this band increases with an increase of the concentration of chromium ions. Strong absorption bands in the field of 1640-1635 cm⁻¹ and 1390-1385 cm⁻¹ are assigned to symmetric and asymmetric valence vibrations of carboxylate-ions, which testifies to the formation of chromium humates. The absorption bands in the field of 1620-1615 cm⁻¹ are characteristic for vibrations of conjugated double bonds C=C of the aromatic fragments. It is noteworthy that overlapping of this band and the absorption band of carboxylate-ions takes place. In the field of 1275-1270 cm⁻¹ absorptions of phenolic OH-groups at 1050-1045 cm⁻¹, deformation vibrations of alcohol hydroxylic groups, are observed. Most remarkable differences are observed in the field of 960-950, 925-920, 825-820, 780-775, 620-615, 550-545, 480-475 and 425-420 cm⁻¹, characterizing the vibrations of coordination bonds of oxygen atoms of carboxylic, phenolic and quinoid groups in the complex compounds.

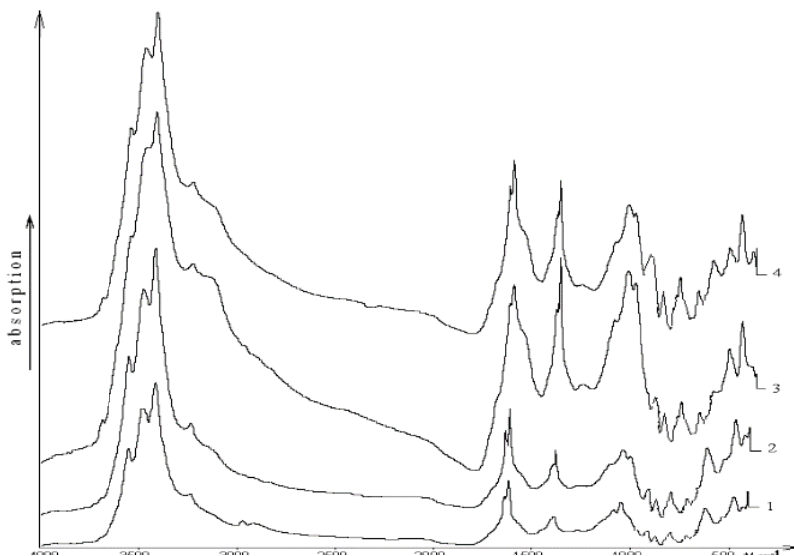


Figure 2– The IR-spectra of the studied samples, obtained with the concentration of chromium ions, %: 1 – 0,005; 2 – 0,07; 3 – 0,1; 4 – 0,5

The influence of the concentration of chromium ions upon the structure of the obtained products has been studied by the method of thermal analysis (figure 3). On DTA curves the following effects are marked: a small endothermic decay at 60°C is connected with the start of the process of extraneous moisture evaporation and removal of occluded gasses; a considerable endo-effect at 120°C is stipulated by dehydration processes; exothermic effects in the field of 310, 345 and 410°C are caused by breaking of a macromolecule of humates and oxidation of the aliphatic part, i.e. removal of hydrocarbon and acid-containing groups from the structure proceeds; heat effects at 430 and 550°C are connected with the breaking

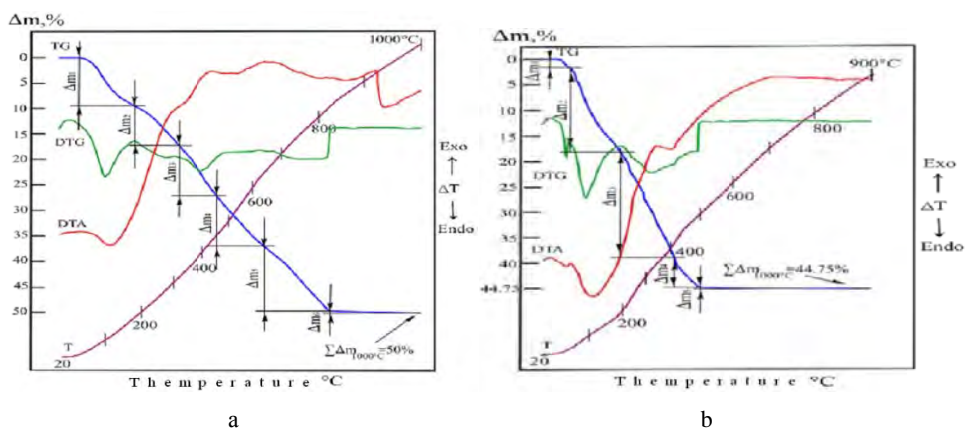
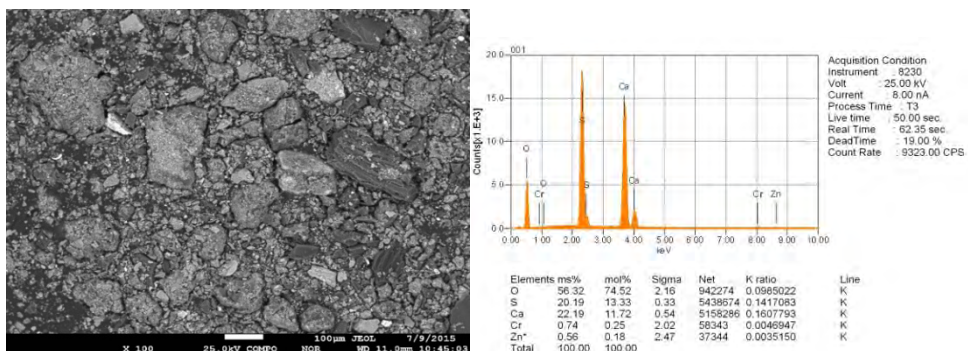


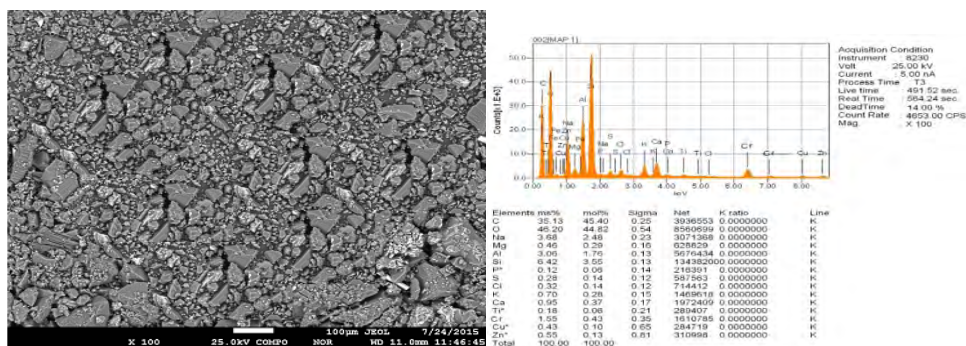
Figure 3 – Thermograms of the studied samples, obtained with different concentration of chromium chloride, %: a – 0,005; b – 0,1

of the side chains, the start of breaking of the aromatic structures [12, 13]. Heat effects in the field of 940°C are caused by the destruction of the mineral part and formation of metal oxide. On the basis of an analysis of thermal destruction of the new complex compounds it has been established that in different temperature fields Me-O bond produces a different effect upon the dynamics of isolation of volatile substances upon the thermal destruction of chromium humates. Herewith, a number of temperature fields have been found, in which a preferable proceeding of a certain type of reactions, connected with the breaking of this or that bond type, is observed. It has been established that an intensive decomposition of chromium humates starts at 310°C and a complete burning-out occurs at 550°C.

Figure 4 provides electronic microscopic shots of the studied samples, which are represented by grains of different sizes. At electronic microphotos (figure 4a) small and large particles of different sizes (3-270 mkm) are seen. Most of them represent agglomerates of still smaller particles. The form of the particles is mainly irregular. It follows from the results of EMF-mapping that the content of chromium makes up 0,74 weight %. The sample, obtained upon the interaction of sodium humate with 0,1% of chromium chloride solution (figure 4б), is represented by the aggregates, consisting of small particles of different sizes (3-102 mkm).



a



b

Figure 4 – Electronic microscopic shot of the obtained samples, obtained with different concentration of chromium chloride, %: a – 0,005; b – 0,1

Rare large particles of heavy fraction are observed. A crystalline particle of heavy fraction has been identified by the EDS method. The results of elemental analysis have shown that the content of chromium makes up 1,55 weight %.

In the course of the conducted works it has been established that with increasing of the humate rate from 0,1 up to 1,0 g the yield of humic substances increases (figure 5a). For example, upon the interaction of 0,1% of chromium chloride solution with 0,1 g of humate the yield of humic acids makes up 17,02%, and upon the use of 1,0 g it attains 35,95%. It follows from the analysis of the obtained data (figure 5б), that with increasing of the humate rate from 0,1 up to 0,70 g the mass fraction of chromium increases from 0,88 up to 4,20%, and the further increasing of the humate rate up to 1,0 g results in a decrease of the content of chromium down to 3,46%. Probably, herewith, a desorption of chromium ions occurs.

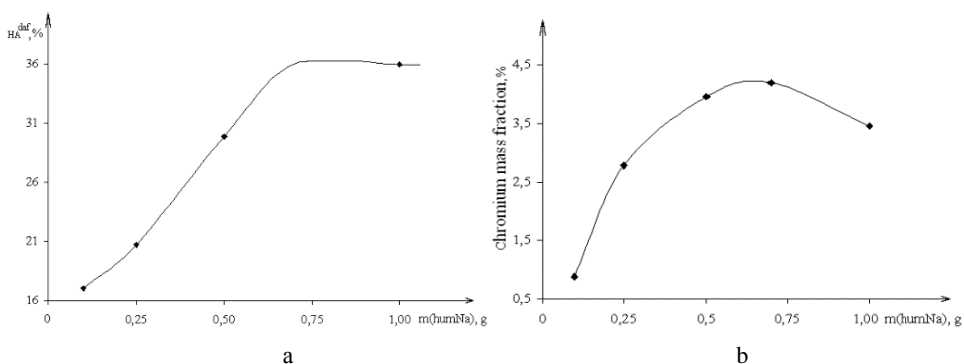


Figure 5 – An isotherm of the dependence of the yield of humic acids (a) and chromium mass fraction (б) upon the sodium humate rate

It has been revealed that with increasing of the humate rate an increase of pH is observed (table 3). Thus, upon the interaction of chromium chloride with 0,1 g of humate pH makes up 4,51, and with 1,0 it attains 7,44. It seems that with increasing of pH of the medium the viscosity of the humate solution decreases, herewith, the extent of their aggregative character decreases, i.e. the colloid aggregates of humic compounds become smaller in sizes and due to this fact they become more movable. As a result the velocity of the interaction of the initial components increases, which leads to an increase in the velocity of the formation of the complex humic compounds of chromium.

Table 3 – Changing of pH in dependence of the concentration of chromium ions

Humate rate, g				
0,10	0,25	0,50	0,70	1,00
4,51	4,69	5,78	6,45	7,44

It is seen from the functional analysis data, provided in Table 4, that in the interaction reactions of sodium humate with chromium ions, different functional groups take part. It has been established that in all studied samples with increasing of the humate rate the content of chromium, bound with the carboxylic and phenolic groups, increases. Thus, the number of carboxylic groups, bound with chromium, increases from 0,38 up to 0,47 mg-eq/g, and the content of the phenolic groups, bound with chromium, increases from 1,50 up to 1,60 mg-eq per 100 g of organic mass. It is noteworthy that under conditions of the conducted studies both the carboxylic and phenolic groups interact partially with chromium ions. Probably, other functional groups of the humic compounds also participate in the reactions.

Table 4 – The influence of sodium humate upon the content of the functional groups in the obtained samples

m (HumNa), g	Content of acidic groups, mg-eq/g		
	COOH	OH _{phen.}	COOH+ OH _{phen.}
0,10	0,38	1,50	1,88
0,25	0,39	1,52	1,91
0,50	0,43	1,55	1,98
0,70	0,46	1,59	2,05
1,00	0,47	1,60	2,07

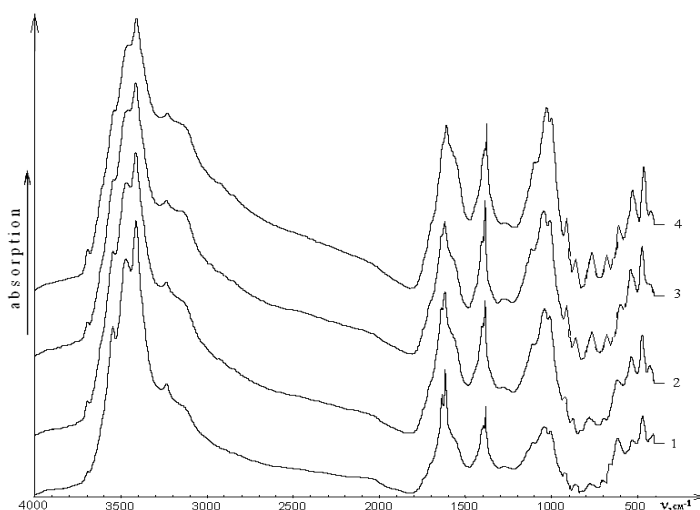


Figure 6 – The IR-spectra of the studied samples, obtained with the humate rate of: 1 – 0,1; 2 – 0,5; 3 – 0,7; 4 – 1,0 g.

The IR-spectra of the studied samples, provided in figure 6, show the complexity of their composition: strong and intensive absorption bands at 3550-3545, 3475-3470, 3420-3415 and 3290-3280 cm^{-1} correspond to valence vibrations of

OH- and NH-groups, bound by intermolecular hydrogen bonds, and those at 1620-1615 and 1390-1380 cm^{-1} correspond to asymmetric and symmetric vibrations of the ionic form of carboxylic groups. An increase of their intensity is connected with the overlapping of surface vibrations of C=C-bonds of the aromatic structures at 1620-1610 cm^{-1} . The absorption bands in the field of 1275-1270 cm^{-1} are characteristic for the deformation vibrations of OH-groups of phenols, -C-O-groups of aromatic carboxylic acids and complex esters, the absorption bands in the field of 1050-1045 cm^{-1} are characteristic for the deformation vibrations of OH-groups of alcohols. The absorption bands of average intensity in the field of 960-955, 925-920, 830-825, 780-770, 620-615, 545-540, 475-470 and 425-420 cm^{-1} confirm the formation of Me-O bond in the complex humic compounds with chromium. It has been established that an intensity of the indicated absorption bands increases with increasing of the humate rate.

Conclusions. The regularities of the influence of the concentrations of chromium ions and the humate rate upon the interaction process of humate and chromium have been revealed. It has been shown that increasing of the specified parameters contribute to an increase in the yield of humic substances up to 36,49% and chromium mass fraction up to 4,31%. The formation of complex compounds of humates with chromium ions has been established by the chemical-physical and chemical methods. Shifting of pH to the acidic field and the absorption bands in the field of 960-955, 925-920, 830-825, 780-770, 620-615, 545-540, 475-470 and 425-420 cm^{-1} confirm the formation of Me-O bond in the complex humic compounds with chromium ions. It has been established that the introduction of chromium ions into the structure of humic compounds is accompanied by more intensive processes of oxidation of organic molecule of humates to the extent of their complete burning-out.

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Резюме

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Cr (III) ИОНДАРЫНЫҢ НАТРИЙ ГУМАТЫМЕН СУЛЫ ОРТАДА ӘРЕКЕТТЕСУІ

Натрий гуматының хром (III) хлоридімен әртүрлі жағдайларда әрекеттесу заңдылықтары зерттелді. Химиялық талдау және физика-химиялық (ИКС, ДТТ, РЭМ) әдістермен гуматтардың хром иондарымен кешенді қосылыстар түзетіндігі айқындалып, алынған үлгілердің құрамы мен қасиеттері анықталды.

Түйін сөздер: натрий гуматы, хром хлориді, кешен түзу, функциональды топтар.

Резюме

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ВЗАИМОДЕЙСТВИЕ ИОНОВ Cr (III) С ГУМАТОМ НАТРИЯ В ВОДНЫХ РАСТВОРАХ

Исследованы закономерности процесса взаимодействия гуматанатрия с хлоридом хрома (III) при различных условиях. Химическим анализом и физико-химическими методами (ИКС, ДТА, РЭМ) установлено образование комплексных соединений гуматов с ионами хрома, определены состав и свойства полученных образцов.

Ключевые слова: гумат натрия, хлорид хрома, комплексообразование, функциональные группы.