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Д.В. Сокольский атындағы «Жанармай,
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ИЗВЕСТИЯ

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК
РЕСПУБЛИКИ КАЗАХСТАН
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NAS RK is pleased to announce that News of NAS RK. Series of chemistry and technologies scientific journal has been accepted for indexing in the Emerging Sources Citation Index, a new edition of Web of Science. Content in this index is under consideration by Clarivate Analytics to be accepted in the Science Citation Index Expanded, the Social Sciences Citation Index, and the Arts & Humanities Citation Index. The quality and depth of content Web of Science offers to researchers, authors, publishers, and institutions sets it apart from other research databases. The inclusion of News of NAS RK. Series of chemistry and technologies in the Emerging Sources Citation Index demonstrates our dedication to providing the most relevant and influential content of chemical sciences to our community.

Қазақстан Республикасы Ұлттық ғылым академиясы "ҚР ҰҒА Хабарлары. Химия және технология сериясы" ғылыми журналының Web of Science-тің жаңаланған нұсқасы Emerging Sources Citation Index-те индекстелуге қабылданғанын хабарлайды. Бұл индекстелу барысында Clarivate Analytics компаниясы журналды одан әрі the Science Citation Index Expanded, the Social Sciences Citation Index және the Arts & Humanities Citation Index-ке қабылдау мәселесін қарастыруды. Web of Science зерттеушілер, авторлар, баспашилар мен мекемелерге контент тереңдікі мен сапасын ұсынады. ҚР ҰҒА Хабарлары. Химия және технология сериясы Emerging Sources Citation Index-ке енүі біздің қоғамдастық үшін ең өзекті және беделді химиялық ғылымдар бойынша контентке адалдығымызды білдіреді.

НАН РК сообщает, что научный журнал «Известия НАН РК. Серия химии и технологий» был принят для индексирования в Emerging Sources Citation Index, обновленной версии Web of Science. Содержание в этом индексировании находится в стадии рассмотрения компанией Clarivate Analytics для дальнейшего принятия журнала в the Science Citation Index Expanded, the Social Sciences Citation Index и the Arts & Humanities Citation Index. Web of Science предлагает качество и глубину контента для исследователей, авторов, издателей и учреждений. Включение Известия НАН РК в Emerging Sources Citation Index демонстрирует нашу приверженность к наиболее актуальному и влиятельному контенту по химическим наукам для нашего сообщества.

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**OBTAINING DERIVATIVES OF HUMIC SUBSTANCES FROM
OXIDIZED COAL AND STUDY OF PHYSICO-CHEMICAL
AND ADSORPTION PROPERTIES**

Abstract. In the work, a chemical analysis of humic substances based on oxidized coal of the Maikuben basin (Kazakhstan) is carried out. Humic acids were obtained on the basis of potassium humates by acidification with a 20% acid solution to pH = 3-4.5. The optimal conditions for obtaining nitrohumic acids from oxidized coals are: the duration of the process is 3 hours, the ratio of S:L = 1:5, the content of nitric acid is 64%, sulfuric acid is 96% and the composition of the nitrating mixture is 1:1 (g/g). Amminohumic derivatives were obtained in the presence of a 3% aqueous solution of ammonia using mechanical activation and ultrasonic treatment. The samples obtained were tested as an adsorbent for water purification from heavy metals. Humic acids and amminohumate showed the highest degrees of purification for zinc (99.0-100.0%) and cadmium (80.0-96.7%), and nitrohumic acid showed a high adsorption capacity for heavy metals like copper - 100.0 % and lead 82.9%. This is due to the fact that when interacting with heavy metals, humic acids and their derivatives (amino and nitro) form chelate complexes due to carboxyl, phenolic, nitro and amino groups. As a result of the study, the possibility of using them as non-toxic available sorbents for the purification of heavy metals in aqueous media has been shown.

Key words: oxidized coal, humic acid, nitrogumic acid, amino humate, adsorbent, heavy metals.

Humic substances (HS) are a macrocomponent of organic matter in soil and water ecosystems, as well as solid fossil fuels. The use of brown and oxidized bituminous coals for the production of humic fertilizers and plant growth stimulants is one of the promising directions in coal chemistry. For humic acids (HA) coals are characterized by a general type of composition and structure. However, depending on the initial composition of coal, the method of extraction and storage, the indicators of their composition and structure may vary. The physiological activity of HA is largely due to the content of quinoid groups and phenolic hydroxides [1].

The presence in the macromolecules of oxidized carbons and humic acids of an aromatic framework, highly substituted by functional groups such as carboxyl, phenolic, quinoid, carbonyl and others, determines their ability to enter into an ion exchange reaction and the possibility of using them as sorbing substances [2].

To increase the efficiency of humic preparations in sorption processes, their directed functionalization seems to be promising, in particular, by introducing nitro-, amino- and other groups into their composition. Interest in such sorbents is caused by the combination of ion-exchange properties with respect to alkali and alkaline earth metals and the possibility of complexation with transition metals. A significant contribution to the complexation is made by nitrogen atoms, which, in contrast to oxygen atoms, have a higher polarizability and are more prone to the formation of donor-acceptor bonds with metal ions [3].

Nitrohumic acids have received considerable attention as potential soil amendments for nitrogen fertilizers and many other applications, such as plant biostimulants and chelating agents for metals [4-7],

as they are characterized by high sorption and complexing properties. They are usually produced by basic coal mining that has been oxidized with nitric acid.

Aromatic nitration, discovered by Mitscherlich in 1834, is a typical electrophilic substitution reaction. The electrophile is the nitronium cation NO^{2+} . The nitronium ion has a linear structure, the nitrogen atom is in the sp^1 state, and oxygen is in the sp^2 hybridization state [8].

Humic substances (HS), in addition to being a source of C and N for microorganisms and plants, are important in the chemical and physical properties of the soil, mainly due to their high complexing ability with respect to metal ions, which is a consequence of the presence of oxygen-containing functional groups in their structure associated with their high specific surface [9, 10].

It is known that the coals of humic acids are weakly acidic cation exchangers. When nitrogen atoms are more prone to donor-acceptor bonds with metal ions than oxygen atoms are introduced into these carbons, the latter become more complex and polyampholytic [11].

Methods for introducing nitro and amino groups into the composition of coals or humic acids (HS) are their direct nitration or amination.

The aim of the work is to obtain nitro-, amino-humic substances from oxidized coal of the "Maikuben" basin and to study their physicochemical and adsorption properties.

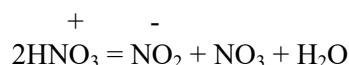
The raw material used was brown coal from the Maikuben deposit, pre-crushed to a particle size of less than 0.1 mm and having the following characteristics (wt%): A^d - 25.8; W^r - 9.3; V^d - 46.6; S_t^d - 0.71. The yield of free humic acids was (on the analytical state) - 87%.

The moisture, ash content and volatility of the samples were determined on a "Thermoster Eltra" thermogravimetric analyzer (according to ASTM D7582-12). The total pore volume, bulk density, pH of the aqueous extract, adsorption activity for methyl orange and methylene blue were determined in accordance with the procedures [12, 13]. The adsorption characteristics of the sorbents (specific surface area) were studied by the Brunauer-Emmett-Teller (BET) method, measurements were carried out on a KATAKON Sorbtometer M. Chemical analysis and surface morphology were studied by energy dispersive X-ray spectroscopy using an SEM instrument (*Quanta 3D 200i*) with an *EDAX* energy dispersive analysis attachment. The IR spectrum of the samples was recorded on a Nicolet iS 10 FT-IR spectrometer.

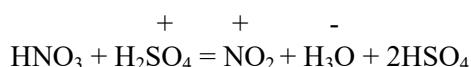
Humic substances are obtained from oxidized brown coal, purified and determined in accordance with the recommendations of the International Humic Substances Society (IHSS). Humic acids were obtained on the basis of potassium humates, by acidifying them with a 20% acid solution to $\text{pH} = 3 - 4.5$, as a result of the reaction, humic acids precipitated in the form of amorphous brown sediments.

Nitrohumic acids were obtained according to the method described in [2], where coal was treated with 64% nitric acid and 96% sulfuric acid in a ratio of 1: 1 (g / g) in a cooled flask. The ratio S:L was 1: 5. The coal nitration method using a nitrating mixture is the most effective. Sulfuric acid has a catalytic effect and reduces the oxidative effect of nitric acid. The nitrating mixture was added to the moistened charcoal in small portions with vigorous stirring and cooling. The process was carried out at a temperature not higher than 40-50 °C to suppress oxidative reactions, the duration of the experiment was 3 hours. The precipitate was separated from the filtrate, washed several times with water, and dried. The nitrocarbon yield was 85%. Nitrohumic acid was obtained from nitrocarbon by alkaline treatment (3% KOH, microwave treatment for 6-7 min, power 1000 W) and subsequent precipitation with 5% acid solution.

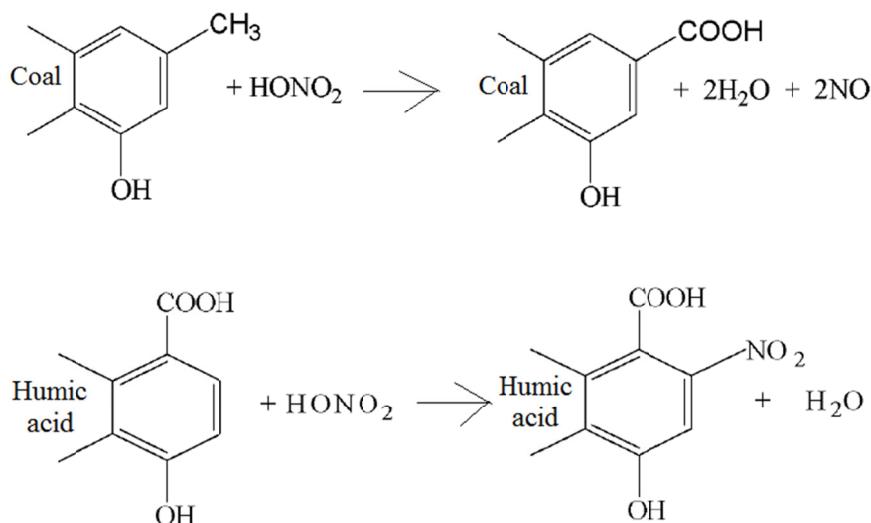
The nitrating agent is nitronium ions, which are formed during the decomposition of concentrated nitric acid:



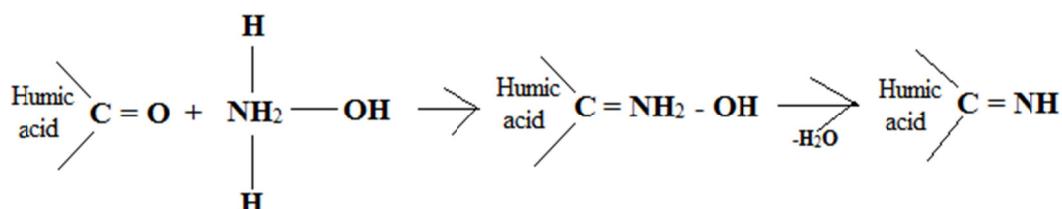
or in the interaction of sulfuric and nitric acid:



Nitration of coals occurs similarly to aromatic hydrocarbons by the mechanism of electrophilic substitution for the aromatic nucleus of carbon macromolecules and leads to the formation of nitrohumic acids [1].



To obtain aminogumic substances, oxidized coal was crushed to 2.95-452 microns. Then, in a rotary-pulsating apparatus (RPA), it was subjected to intensive oxidation and dispersion of coal particles with atmospheric oxygen, the mixture was heated to 50 °C and brought to an ultrafine state and a homogenized mass in the presence of a 3% aqueous ammonia solution for 20 minutes. After RPA, the finished mass was fed into the extraction vessel for holding the solution for 1 hour. The aged solution was fed to the synthesis module for ultrasonic dispersion, where it was subjected to ultrasonic dispersion at a certain frequency. The ultrasonic treatment time was 25 minutes.



To carry out research on the removal of heavy metals using humic substances, a model solution of heavy metals (copper, zinc, lead, cadmium) was prepared from state standard samples (SSS). In a conical flask (250 ml), a weighed portion of the sorbent (0.5 g) was stirred with a model solution (50 ml, pH = 3.26) and stirred in a shaker at room temperature (25°C) at a stirring speed of 200 rpm for 3 hours. After the process, humic substances with heavy metals were extracted from the solution by filtration. The solution filtered from the adsorbent was analyzed for the content of heavy metals on a Ta-lab voltammetric analyzer.

The chemical composition and physicochemical characteristics of the obtained humic substances are shown in tables 1-3.

Table 1 - Chemical composition of humic substances

№	Denomination	Content of elements, wt.%										
		C	O	Na	Mg	Al	Si	K	Fe	Ca	S	Ti
1	Humic acids	19.47	40.03	-		0.72	0.58	38.06	1.15	-	-	-
2	Nitrohumic acids	50.51	29.19	0.17	0.22	3.45	9.46	0.70	1.69	-	0.19	-
3	Aminohumate	56.09	31.08	0.19	0.30	2.84	7.25	0.65	0.74	0.49	-	0.36

According to the data obtained, it should be noted that the potassium content (38.06%) in comparison with the initial humic acid decreases to 0.70% and 0.65% in the derivatives of nitrogumic and aminohumic acids, respectively, which may be due to the replacement of potassium ions by amino and nitro groups.

Table 2 - Content of functional groups of humic substances

No	Denomination	Carboxyl groups meq / g	Total acidity, meq / g	Phenolic group, meq / g
1	Humic acids	1,18	1,60	0,42
2	Nitrohumic acids	0,60	1,64	1,04
3	Aminohumate	0,12	0,73	0,61

The data in table 2 show a 50 % decrease in carboxyl groups from the original form of humic acid in the derivatives of humic acids. The nitro and amino groups increase the reactivity of other substituents on the aromatic ring. It should be noted that in aromatic acids nitration often occurs the substitution of the carboxyl group for nitro and amino groups.

Table 3 - Physical and chemical characteristics of the obtained humic substances

No	Denomination	W ^r ,%	A ^r ,%	V ^d , %	S _{BET} , m ² /g	ρ _{bulk} , g /cm ³	V _Σ by water, cm ³ /g	pH	A _m , mg/g	A _{m.b.} , mg/g
1	Humic acids	13.32	25.73	62.25	0.42	0.95	-	4,09	28,0	-
2	Nitrohumic acids	5,52	57,87	67,93	5.637	0,882	0,43	6,60	-	-
3	Aminohumate	3,41	74,13	56,77	3.940	0,857	0,17	10,07	45,5	112,5

Figure 1 shows the IR spectrum of humic acid, peaks were found in the region of 2918 cm⁻¹, which can be associated with CH stretching vibration of alkyl chains, which can also be a broad signal N - H/O - H. Peak at about 1701 cm⁻¹ typical for the stretching vibration of C = O carbonyl groups of ketones (including quinones), carboxylic acids and / or amides. The band of deformed stretching vibrations in the region of 1650-1520 cm⁻¹ also indicates the presence of a strong N-H group. The peak in the 1100-1000 cm⁻¹ range is responsible for the strong elongation of the C-O group.

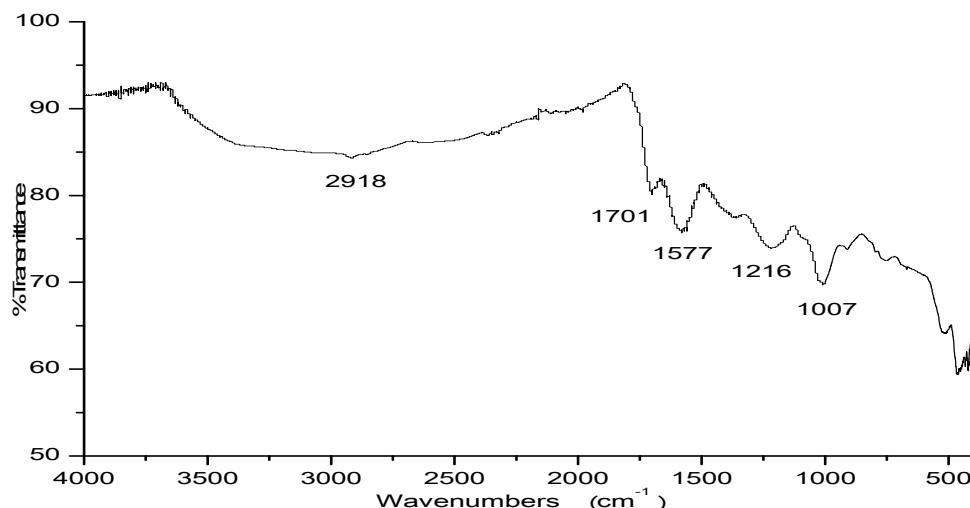


Figure 1 - IR spectrum of humic acid

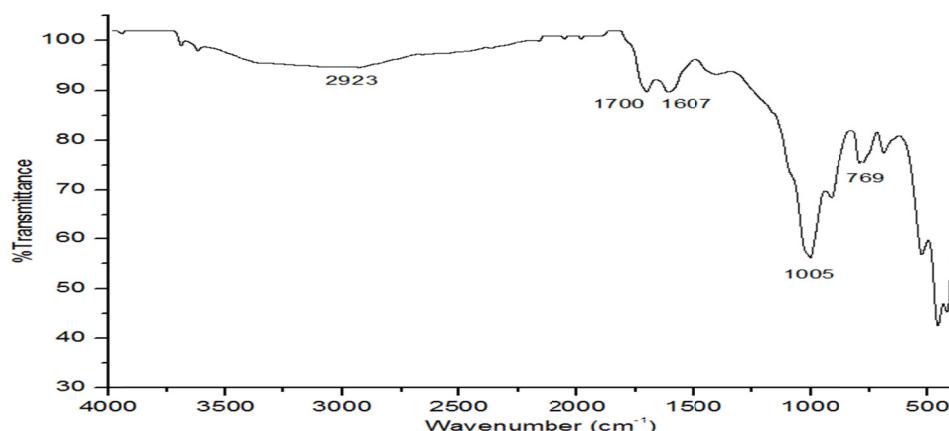


Figure 2 - IR spectrum of nitrohumic acids

In Figure 2, the absorption bands in the range of wavenumbers 3700-3300 cm⁻¹ refer to weak stretching vibrations of O – H bonds, probably due to the presence of moisture in this compound. In the region of 2923 cm⁻¹ to be associated with C-H stretching vibration of alkyl chains. A peak at about 1700 cm⁻¹, typical of the C = O stretching vibration of carbonyl groups of ketones (including quinones), carboxylic acids and / or amides, confirms that these units are present in humic acid. The peak in the 1100-1000 cm⁻¹ range is responsible for the strong elongation of the C-O group. The wide range of peak variation from 800-650 cm⁻¹ can be explained by the tensile C-H vibration. Peak 920-830 cm⁻¹ for nitroparaffin compounds, 1560-1500 cm⁻¹ for aryl groups.

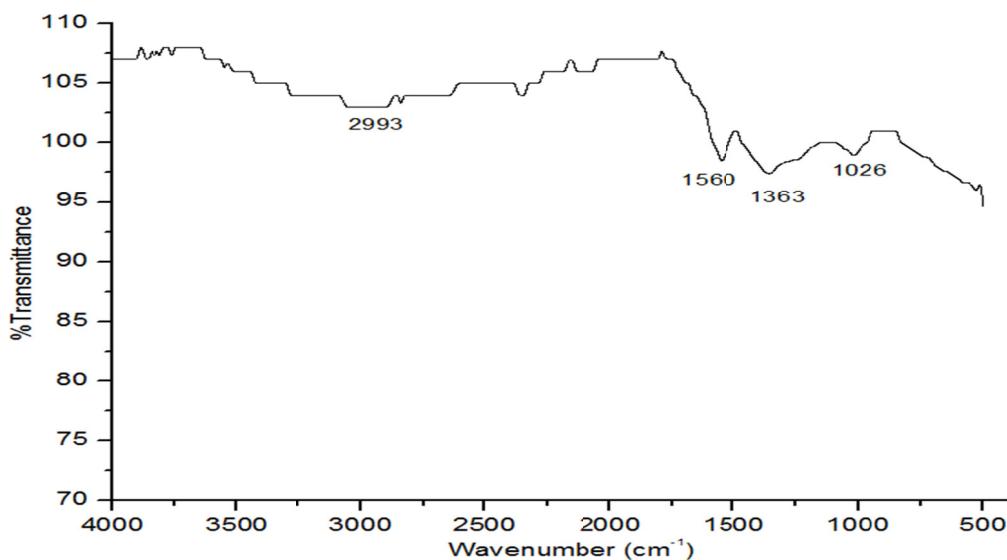


Figure 3 - IR spectrum of amino humate

Figure 3 shows a peak at 2993 cm⁻¹, which is responsible for the presence of aromatic stress assigned to C-H. There is also a slight shift of the band at 1576 cm⁻¹, which also indicates the presence of a strong N – H group. The peak at 1560 cm⁻¹ is characterized by asymmetric and 1363 cm⁻¹ symmetric tensile vibration of aromatic tertiary amines. The peak in the 1100-1000 cm⁻¹ range is responsible for the strong elongation of the C-O group.

The particle size of the amino humate was determined using the Mastersizer 3000. The frequency results are shown in Figure 4. The particle size of the amino humate was 10% - 0.687 µm, 50% - 7.21 µm, 90% - 296 µm.

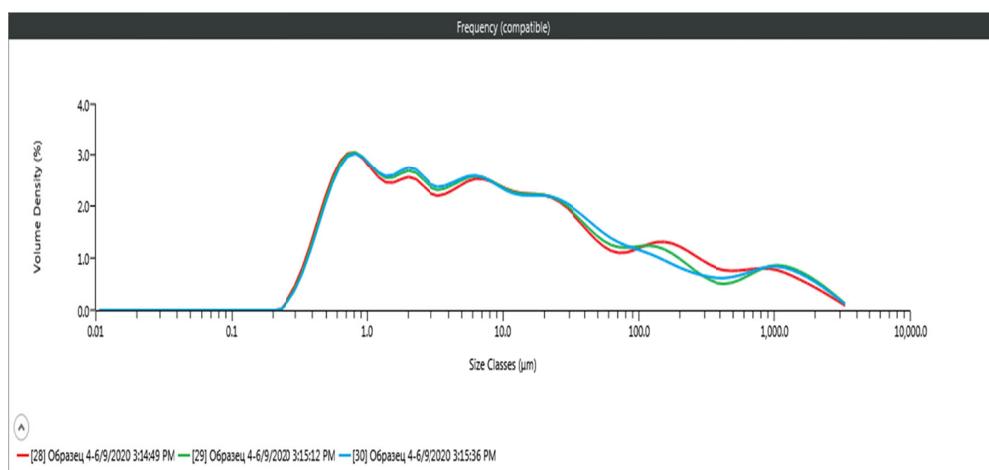


Figure 4 - Particle size of amino humate

The obtained HS were tested for water purification from heavy metals. Analysis of the data obtained showed that after water purification, the values of all heavy metals decrease (table 4).

Table 4 - Testing of humic substances for water purification from heavy metals

Heavy metals, mg/l	$C_0(\text{Me}), \text{mg/l}$	Humic acids		Nitrhumic acids		Aminohumate	
		$C_{\text{residual}}(\text{Me}), \text{mg/l}$	Purification degree, %	$C_{\text{residual}}(\text{Me}), \text{mg/l}$	Purification degree, %	$C_{\text{residual}}(\text{Me}), \text{mg/l}$	Purification degree, %
Zinc	0.10 ± 0.01	0.0010 ± 0.0004	99.00	0.052 ± 0.009	48,00	Item not found	100,00
Cadmium	0.10 ± 0.01	0.0033 ± 0.0003	96.70	0.10 ± 0.03	-	0.020 ± 0.005	80,00
Lead	0.10 ± 0.01	0.0216 ± 0.0005	78.40	0.015 ± 0.004	85,00	0.036 ± 0.009	64,00
Copper	0.10 ± 0.01	0.0171 ± 0.0003	82.90	Item not found	100,00	0.1 ± 0.01	-

As a result of sorption, the obtained humic substances removed most of the heavy metals from the solution and showed a high degree of purification. Humic acids and aminohumate showed the highest degrees of purification for zinc (99.0-100.0%) and cadmium (80.0-96.7%), and nitrogumic acid showed a high adsorption capacity for heavy metals like copper - 100.0 % and lead 82.9%. This is due to the fact that when interacting with heavy metals, humic acids and their derivatives (amino and nitro) form chelate complexes due to carboxyl, phenolic, nitro and amino groups.

Thus, nitro- and amino-humic substances were obtained from the oxidized coal of the Maikuben deposit by nitration and amination. Their physicochemical and adsorption properties have been studied. As a result of the study, the possibility of using them as non-toxic available sorbents for the purification of heavy metals in aqueous media has been shown.

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ТОТЫҚҚАН ҚӨМІРДЕН ГУМИНДІ ЗАТ ТҮҮНДҮСІСИН АЛУ ЖӘНЕ ФИЗИКА-ХИМИЯЛЫҚ, АДСОРБЦИЯЛЫҚ ҚАСИЕТТЕРІН ЗЕРТТЕУ

Аннотация. Жұмыста Майқебе бассейні (Қазақстан) тотықкан қөмір негізінде алынған гуминді заттарға химиялық талдау жүргізілді. Гумин қышқылдары калий гуматынан 20% қышқыл ерітіндісімен pH = 3-4,5 дейін қышқылдандыру арқылы алынды. Тотықкан қөмірден нитрогумин қышқылдарын алудың онтайлы шарттары: үдерістің ұзақтығы – 3 сағат, қатынасы k:c=1:5, азот қышқылының концентрациясы 64%, күкірт қышқылы 96% және нитратта арналған қоспасын құрамы 1:1 (г/г). Нитрат қоспасын қолдану арқылы қөмірді нитраттау әдісі тиімді болып саналады. Күкірт қышқылы каталитикалық әсерге ие және азот қышқылының тотығу әсерін азайтады. Қөмірдің нитрленуі ароматикалық қөмірсутектер сияқты қөмірдің макромолекула-сының ароматикалық ядроны бойынша электрофильді алмастыру механизміне сәйкес жүреді және нитрогумин қышқылдары пайда болады. Нитрат қоспасы қарқынды араластыру және салқыннату кезінде ылғалданған қөмірге қосылды. Процесс тотығу реакцияларын басу үшін 40-50 °C аспайтын температурада жүргізілді, тәжірибелі ұзақтығы 3 сағатты құрады. Тұнба фильтрттадан бөлініп, бірнеше рет сумен жуылды және кептірілді. Нитрокөмір шығымы 85% құрады. Нитрогумин қышқылын нитрокөмірден сілтілік өндеу арқылы (3% KOH, микротолқынды пеште 6-7 мин бойы өндеу, құаты 1000 Вт) және одан кейін 5% қышқыл ерітіндісімен тұндыру арқылы алды.

Амминогумин туындылары механоактивация және ультрадыбыстық тұрғыда өндей отырып, аммиактың 3% сулы ерітіндісінің қатысуы негізінде алынды. Амминогуминді заттарды алу үшін тотықкан қөмір 2,95-452 мкм дейін ұсақталды. Одан әрі роторлы-пульсациялық аппаратта (РПА) қөмір бөлшектері ауа оттегі қатысында қарқынды тотығуға және диспергирлеуге ұшырады, қоспа 50°C дейін қыздырылды және 20 минут ішінде аммиактың 3% сулы ерітіндісінің қатысуы арқылы ультрадисперсті күйге және гомогенделген массага дейін жеткізілді. РПА-дан кейін дайын масса ерітіндіні 1 сағат ұстасу үшін экстракция ыдысына берілді. Ұсталған ерітінді ультрадыбыстық диспергацияға арналған синтез модуліне жіберілді, онда ол белгілі бір жайлікте ультрадыбыстық диспергирлеуге ұшырады. Ультрадыбыстық өндеу уақыты 25 минутты қорсетті. Гуминді заттарды қолдана отырып, ауыр металдан тазарту бойынша зерттеулер жүргізу үшін мемлекеттік стандартты үлгілерден (ГСО) ауыр металдардың модельдік ерітіндісі (мыс, мырыш, қорғасын, кадмий) дайындалды. Конустық колбада (250 мл) сорбент (0,5 г) модельдік ерітіндімен (50 мл, pH=3.26) араластырылды және шейкерде бөлме температурасында (25°C), араластыру жылдамдығы 200 айн/мин, 3 сағат бойы араластырылды. Процесті жүргізгеннен кейін ерітіндіден ауыр металдармен гуминді заттар сүзу арқылы алынды. Адсорбенттен сүзілген ерітінді Ta-lab вольтамперометрлік анализаторындағы ауыр металдардың құрамында талданды.

Сорбция нәтижесінде алынған гуминді заттар ерітіндіден ауыр металдардың көп бөлігін алып тастап, тазартудың жоғары дәрежесін қорсетті. Гумин қышқылдары мен аминогумат мырыштан (99,0-100,0 %) және кадмийден (80,0-96,7%) тазартудың ең жоғары дәрежесін қорсетті, ал нитрогумин қышқылы мыс – 100,0% және қорғасын 82,9% сияқты ауыр металдарға жоғары адсорбциялық қабілеттін қорсетті. Ауыр металдармен әрекеттескен кезде гумин қышқылдары және олардың туынды формалары (амин және нитро) карбоксил, фенол, нитро және амин топтарының әсерінен хелат кешенін құратындығы түсіндіріледі. Зерттеу нәтижесінде оларды сулы ортаның ауыр металдарын тазарту кезінде үйтты емес қолжетімді сорбенттер ретінде пайдалану мүмкіндігі қорсетілген.

Түйін сөздер: тотықкан қөмір, гумин қышқылы, нитрогумин қышқылы, аминогумат, адсорбент, ауыр металдар.

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ПОЛУЧЕНИЕ ПРОИЗВОДНЫХ ГУМИНОВЫХ ВЕЩЕСТВ ИЗ ОКИСЛЕННОГО УГЛЯ И ИЗУЧЕНИЕ ФИЗИКО-ХИМИЧЕСКИХ И АДСОРБЦИОННЫХ СВОЙСТВ

Аннотация. В работе представлены результаты химического анализа гуминовых веществ на основе окисленного угля Майкубенского бассейна (Казахстан). Гуминовые кислоты были получены на основе гуматов калия путем подкисления 20%-ным раствором кислоты до pH = 3-4,5. Оптимальными условиями для получения нитрогуминовых кислот из окисленных углей являются: продолжительность процесса 3 часа, соотношение Т:Ж=1:5, концентрация азотной кислоты 64%, серной кислоты 96% и состав нитрующей смеси 1:1 (г/г). Метод нитрования угля с использованием нитрующей смеси является наиболее эффективной. Серная кислота оказывает каталитическое влияние и уменьшает окислительное действие азотной кислоты. Нитрование углей происходит подобно ароматическим углеводородам по механизму электрофильного замещения по ароматическому ядру макромолекул угеля и приводит к образованию нитрогуминовых кислот. Нитрующую смесь прибавляли к увлажненному углю небольшими порциями при интенсивном перемешивании и охлаждении. Процесс проводился при температуре не выше 40-50 °C для подавления окислительных реакций, продолжительность опыта составил 3 часа. Осадок отделяли от фильтрата, промывали многократно водой и сушили. Выход нитроугля составил 85%.

Нитрогуминовую кислоту получали из нитроугля щелочной обработкой (3 % KOH, обработка в микроволновой печи течение 6-7 мин, мощность 1000 Вт) и последующим осаждением 5 % раствором кислоты.

Аминогуминовые производные были получены в присутствии 3 % водного раствора амиака с применением механоактивации и ультразвуковой обработки. Для получения аминогуминовых веществ окисленный уголь был измельчен до 2,95-452 мкм. Далее в роторно-пульсационном аппарате (РПА) подвергался интенсивному окислению и диспергированию частиц угля кислородом воздуха, смесь нагревалась до 50°C и доводился до ультрадисперсного состояния и гомогенизированной массы в присутствии 3 % водного раствора амиака в течение 20 минут. После РПА готовая масса подавалась в емкости экстракции для выдержки раствора в течение 1 часа. Выдержаный раствор подавался в модуль синтеза для ультразвуко-вой диспергации, где подвергался воздействию ультразвуковому диспергированию, определенной частотой. Время ультразвуковой обработки составил 25 минут. Для проведения исследований по очистке от тяжелых металлов с применением гуминовых веществ, готовился модельный раствор тяжелых металлов (медь, цинк, свинец, кадмий) из государственных стандартных образцов (ГСО). В конической колбе (250 мл) размешивали навеску сорбента (0,5 гр) с модельным раствором (50 мл, pH=3.26) и перемешивали в шейкере при комнатной температуре (25°C), при скорости перемешивания 200 об/мин в течение 3 часов. После проведения процесса, из раствора гуминовые вещества с тяжелыми металлами извлекали путем фильтрации. Отфильтрованный от адсорбента раствор анализировали на содержание тяжелых металлов на вольтамперо-метрическом анализаторе Ta-lab.

В результате сорбции, полученные гуминовые вещества вывели из раствора большую часть тяжелых металлов и показали высокую степень очистки. Гуминовые кислоты и аминогумат показали наиболее высокие степени очистки по цинку (99,0-100,0 %) и кадмия (80,0-96,7 %), а нитрогуминовая кислота показала высокую адсорбционную способность к тяжелым металлам как медь – 100,0 % и свинец 82,9 %. Это объясняется тем, что при взаимодействии с тяжелыми металлами гуминовые кислоты и их производные формы (амино- и нитро-) образуют хелатные комплексы за счет карбоксильных, фенольных, нитро- и амино- групп. В результате исследования показана возможность использовать их в качестве нетоксичных доступных сорбентов при очистки тяжелых металлов водных сред.

Ключевые слова: окисленный уголь, гуминовая кислота, нитрогуминовая кислота, аминогумат, адсорбент, тяжелые металлы.

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REFERENCES

- [1] Orlov D.S., Sadovnikova L.K., Savrova A.L. (1995) Reports of the Academy of Sciences, ser. "Geochemistry"345 (4): 1-3 (in Russ.).
- [2] Zhakina A. Kh., Utegenova A. S., Akkulov Z.G. (2006) Synthesis and ion-exchange properties of nitrohumic acid, Reports of the National Academy of Sciences of the Republic of Kazakhstan, 1: 28-30 (in Russ.).
- [3] Kudaibergen G.K., Akkulova Z.G., Amirkhanov A.K., Zhakina A.Kh., Vasilets E.P., Sadykov O.V. (2015) Sorption of metals by functionalized derivatives of humic acids, Chemical Journal of Kazakhstan, 2: 149 (in Russ.).
- [4] Albuquerque Brocchi E., Dick D.P., Leite A.J.B. (2013) Nitration effect on the yield and chemical composition of humic acids obtained from South Brazil coal samples. In: Xu J, Wu J, He Y, editors, Functions of natural organic matter in changing environment. New York: Springer:1129–1132 (in Eng.).
- [5] Lawson G.J., Stewart D. (1989) Coal humic acids. In: Hayes MHB, MacCarthy P, Malcolm RL, Swift RS, editors. Humic substances II. In search of structure. Chichester: John Wiley & Sons: 641–686 (in Eng.).
- [6] Patti A.F., Verheyen T.V., Douglas L., Wang X.(1992) Nitrohumic acids from Victorian brown coal, Sci Total Environ, 113(1-2): 49–65 (in Eng.).
- [7] Syahren AM, Wong NC. (2008) Extraction and chemical characteristics of nitro-humic acids from coals and composts, J. Trop Agric and Fd. Sc., 36(2): 269–279 (in Eng.).
- [8] V.A. Osyanin Yu.N. Klimochkin (2007) Nitration, Workshop - Samara, Samara State Technical University: 23 (in Russ.).
- [9] Canellas L. P., Santos G. A., Moraes A. A., Rumjanek V. M., Olivares F. L.(2000) Rev. Bras. Cienc. Solo, 24: 741 (in Eng.).
- [10] Passos R. R., Ruiz H. A., Mendonça E. S., Cantarutti R. B., Souza A. P. (2007) Rev. Bras. Cienc. Solo, 31: 1119 (in Eng.).
- [11] Amirkhanova A.K., Akkulova Z.G. (2006) Synthesis and ion-exchange properties of amine derivatives of oxidized coals, Chemistry for sustainable development, 3:215 (in Eng.).
- [12] Farberova E.A., Tingaeva E.A., Maksimov A.S. (2015) Rus. J. Appl. Chem., 88 (4): 579 (in Eng.).
- [13] Uvarov N.F. (2018) Mesoporous carbon materials and their application in capacitive electrochemical devices, V International Farabi Readings: 3 (in Russ.).

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