

## Changes in the Physicochemical Characteristics of Humic Acids in a Hydrodynamic Rotor-Pulsation Apparatus

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### Abstract

The work presents research results of the change comparison of brown coals and the study of the physicochemical properties of humic substances obtained from brown coals of the Karazhyra, Ekibastuz, and Kyzyl-Kiya deposits after hydrodynamic treatment in a rotary-pulsation apparatus. It is shown that the hydromechanical effect on humic acids leads to a change in their composition, accompanied by a decrease in the degree of aromaticity and an increase in the content of oxygen-containing fragments. Mechanical treatment of brown coals under oxidizing conditions maximizes the efficiency of extraction of water-soluble components and humic acids. The structural parameters and functional composition of humic acid molecules during the treatment of brown coals under oxidation-reduction conditions change depending on the conditions. The elemental and functional composition (using IR spectroscopy and potentiometry) of humic substances in brown coals and their molecular weight distribution using size-exclusion chromatography were studied. The influence of the content of metal-binding centers, dispersity, and ash content of humic substances was studied before and after treatment. At a temperature of 70 °C a rotation time of 10 s, 98.7% of humic acids passes into the solution, which is the best indicator.

### 1. Introduction

The problem of our agricultural production in the Republic of Kazakhstan is related to soil humus, which is the main source of fertility for any soil. Irrigated soils of the Central Asian region contain very little organic matter; in terms of the amount of humus they are in the very last place among other soils. A meter layer of fertile land per hectare contains 350–700 t of humus, as the best soils of the cotton zone – grey soil contains 65–85 t. The best organic fertilizer is manure, but it is not enough to apply to all cultivated areas that need organic fertilizers.

Another problem in the region's agricultural production is saline lands. Along with the need to develop effective measures for soil desalinization, it is also promising to create fertilizers with ion-ex-

change properties that would help plants grow on saline soils.

One of the alternative sources of replenishment of organic matter in irrigated soils can be brown coals, as well as carbon-humic fertilizers obtained by treating brown coals with various alkalis. The use of brown coals, peat, and other caustobioliths for the production of organomineral fertilizers has long been of interest to agricultural scientists. Caustobioliths are important sources of nitrogen and some other chemical elements useful for plants (potassium, magnesium, zinc, copper, iron, manganese), good ion exchangers, and structure formers. However, not all coals are suitable for producing fertilizers. Wind-blown brown coals contain from 40 to 84% humic acids; in addition to the commonly found iron, magnesium, calcium, potassium, phosphorus, sulfur, and fluorine, trace elements such as zinc, cobalt, copper, molybdenum, manganese, and nickel are found in oxidized coals.

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One of the tasks of our work is a selection of raw materials for the production of salts of humic acids (humates) for the national economy. From this point of view, the raw material should not only contain a large amount of humic acids but should also be easily extracted with alkali. Sodium hydroxide was used as an alkali and a hydrodynamic rotor-pulsation apparatus (HRPA) was used to extract the humate.

The intensification of the process of interaction of alkali with coal to obtain a carbon-alkali reagent and humates was carried out by treating the suspension in a hydrodynamic rotor-pulsation apparatus designed by A.A. Bershitsky and S.P. Tulchinsky, its choice was determined by design features that allow its use in a continuous technological process of large-tonnage production [1].

Depending on the raw material genesis and its metamorphism degree, both low-molecular and high-molecular compounds with different contents of aliphatic and aromatic fragments and functional groups can predominate in the composition of humic acids. Therefore, humic acids isolated from various types of raw materials differ both in composition and properties.

Thus, the presented experimental study results of humic acids' physical- and colloidal-chemical properties indicate the unique properties of this class of natural compounds and, above all, in the field of their application for solving environmental protection and agricultural problems. The high metabolic capacity of humic acids opens up wide opportunities for the production of ion-exchange sorption materials based on them, intended for the purification of waste and process waters from heavy metal ions [2–8], as well as humic preparations for planting desert saline areas [9–12]. The specific conglomerate of properties of humic acids' lipophilic-hydrophilic structure provides this class of natural polymers with the possibility of using them as a selective sorbent of non-polar hydrocarbons in natural environments, reclamation of areas contaminated with non-polar hydrocarbons [13–18].

The high hydrophilicity of humic acids in natural caustobiooliths opens up practically unlimited possibilities for the development of ion-exchange reclamation materials based on them for reclamation of areas disturbed by human economic activities and, above all, areas contaminated with heavy metals and radionuclides [19–23].

Humic acids, as high-molecular systems, are very sensitive to various kinds of physicochemical influences, which, by transforming the fractional and functional composition of their radicals, naturally

give humic preparations new properties. In this regard, the development of methods for the fractionation of humic acids makes it possible to obtain humic preparations that are more effective and more selective in consumer properties [24–29], which is necessary for obtaining standard humic preparations and organizing their industrial production [30–32].

Due to the complexity of humic substances' composition, the nature of the complex-forming centers in them remains unclear [33–35].

One of the ways to modify the structure of humic acids is mechanical treatment of humic substances, which makes it possible to change their structure, content of functional groups, and molecular weight [36–38]. The purpose of this work is a comparative change and study of the physicochemical properties of humic substances obtained from brown coals of the Karazhyra, Ekibastuz, and Kyzyl-Kiya deposits after hydrodynamic treatment in a rotary-pulsation apparatus.

## 2. Research objects and methods

Coal sampling was carried out according to GOST 59248-2020 Brown coals, hard coals, anthracite, oil shales, and coal briquettes. Methods of sampling and sample preparation for laboratory studies.

Brown coals from the Karazhyra, Ekibastuz, and Kyzyl-Kiya deposits were used as research objects. Mechanochemical treatment of coals was carried out in a hydrodynamic rotor-pulsation apparatus (HRPA) designed by A.A. Bershitsky and S.P. Tulchinsky [1]. The experiment was carried out at temperatures from 25 to 70 °C, a rotation time from 3 to 10 s, with NaOH (20%) in the solid ratio: liquid (1:4). The elemental composition of humic acids and fulvic acids was determined on a Carlo Erba Strumentazione model 1106 analyzer (Italy). The functional composition of humic acids was analyzed by IR spectroscopy. The humic acids' spectra were recorded on a Nicolet 5700 IR Fourier spectrometer with a Raman module (Thermo Electron Corporation, USA). Humic substances were isolated from natural objects using alkaline extraction.

## 3. Results and discussion

In order to better understand what is happening to the composition and structure of humic acids under the influence of hydrodynamic treatment, the same treatment was carried out under the most severe conditions: coals with a degree of crushing of 0–3 mm were treated in an HRPA with an alkali

solution at S:L = 1:4 based on 20% alkali per total amount of raw material, temperature 70 °C and duration one minute. After this, the chemical characteristics and fractional composition of the original humic acids and those treated in a HSPA were established. At a temperature of 25 °C a rotation time of 3–5 s, 50% of humic acids pass into the solution. At a temperature of 70 °C a rotation time of 3–5 s, 92.4% of humic acids dissolve. At a temperature of 70 °C a rotation time of 10 s, 98.7% of humic acids passes into the solution, which is the best indicator.

The results (Tables 1 and 2) show that the impact of hydrodynamic forces leads to an increase in the content of carbon and hydroxyl groups in humic acids. The amount of total oxygen of functional groups for humic acids of the Karazhyra and Kyzyl-Kiya coals increases significantly and the oxygen content in an unaccounted form noticeably decreases, which possibly occurs due to the rupture of ether bonds or heterocycles.

During fractionation, the yield of easily salted-out acids noticeably decreases and the yield of

difficult-to-salt-out and non-salted-out acids increases for both humic acids of the Ekibastuz and Karazhyra coal.

During the isothermal decomposition of humic acids in a flow of inert gas (nitrogen) according to the method, it was found that the functional groups of humic acids from three coal samples have different thermal stability. Thus, the decarboxylation of humic acids of the Ekibastuz and Karazhyra brown coals occurs most intensively at a temperature up to 200 °C and is completed at a temperature up to 300 °C, the decarboxylation of humic acids of the wind-blown Kyzyl-Kiya brown coal occurs to an insignificant extent at a temperature up to 200 °C, occurs most intensively and practically ends at the interval of 200–300 °C (Table 3). The elimination of hydroxyl groups is most intense in the first two humic acids in the temperature range of 200–300 °C and at 500 °C remains in insignificant quantities, while from the Kyzyl-Kiya it is most intense in the range of 300–500 °C, after which their content remains significant (0.75 mEq/g).

**Table 1.** Changes in the chemical characteristics of humic acids under the influence of hydrodynamic forces

Humic acids of coals	Elemental composition, % of organic mass					Content of functional groups, mEq/g			Content of oxygen, %		C/H of the hydrocarbon skeleton
	C	H	O	N	S	COOH	OH	CO-carboxyl	In functional groups	In an unaccounted form	
Karazhyra original	60.86	3.86	31.24	0.76	3.46	3.30	4.77	0.95	19.71	11.53	1.28
Karazhyra treated	62.31	3.46	32.90	0.58	0.75	3.30	5.13	0.64	19.79	13.11	1.41
Ekibastuz original	65.70	5.28	26.86	0.74	1.42	2.27	5.81	1.04	18.22	8.64	0.98
Ekibastuz treated	66.15	5.85	26.13	0.59	1.27	2.32	5.97	0.75	18.18	7.95	0.90

**Table 2.** Changes in the fractional composition of humic acids under the influence of hydrodynamic forces

Humic acids	Yield of humic acid fractions, % of total content				
	From original		From treated in the apparatus		
Karazhyra coal					
Salted out	4%		NaCl	19.0	11.0
	5%		NaCl	18.0	12.0
	6%		NaCl	9.0	14.0
	20%		NaCl	12.0	12.0
Ekibastuz coal					
Salted out	6%		NaCl	10.0	5.0
	8%		NaCl	12.0	10.0
	20%		NaCl	17.0	19.0

**Table 3.** Dependence of the content of functional groups in humic acids, original and treated in a hydrodynamic rotor-pulsation apparatus, on temperature

Heating temperature ranges, °C	Content of functional groups in humic acids, mEq/g			
	Original		Treated	
	COOH	OH	COOH	OH
Karazhyra coal				
Initial	3.30	4.77	3.30	5.13
200	0.52	6.63	2.38	4.61
300	-	0.92	0.13	3.65
400	-	0.60	-	0.37
500	-	0.30	-	0.18
Ekibastuz coal				
Initial	2.27	5.81	2.32	5.97
200	0.49	4.16	-	2.97
300	-	0.77	-	0.53
400	-	0.14	-	0.12
500	-	0.14	-	0.15

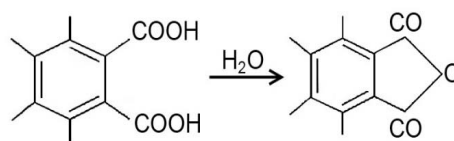
It is known that carboxyl groups at the primary carbon atom are more difficult to destroy than at the aromatic ring. The activation energy of decarboxylation for aliphatic acids is significantly higher than for aromatic acids. In the aromatic ring, decarboxylation of carboxyl groups located in one ring occurs relatively easily. The more electronegative substituents are bonded to the carbon atom adjacent to the carboxyl group, the easier it is to eliminate a carboxyl group.

O- and p-hydroxybenzoic acids easily remove carbon dioxide. Aromatic acids, in which both o-positions to the carboxyl are replaced by metals, remove carbon dioxide especially easily. Hydroaromatic acids are quite easily eliminated.

Based on the foregoing, it can be assumed that the carboxyl groups of humic acids of the Ekibastuz earthy brown coal are located predominantly in alicyclic structures. In the process of mechanochemical destruction, some enrichment of the coal substance with hydrogen occurs and the decarboxylation process is facilitated. It could also be assumed that the carboxyl groups are located predominantly in the o- and p-position relative to the hydroxyl groups in the aromatic ring. However, these humic acids are relatively easily sulfomethylated, which indicates the presence in them of o- and p-positions of the aromatic ring that is unsubstituted concerning the OH-groups. This idea is also confirmed by the fact that in these humic acids the hydroxyl groups, defined as phenolic, begin to degrade at a tempera-

ture up to 200 °C, while the high thermal stability of phenolic hydroxyls, which undergo destruction at temperatures above 400°, is known [2]. Consequently, the decrease in the content of OH-groups occurs due to the destruction of the non-aromatic part of the molecules, to which the isolated aromatic rings containing them are associated. The small content of thermally stable OH-groups indicates an insignificant proportion of their association with condensed aromatic rings.

Decarboxylation of humic acids from the Karazhyra coal, although it seems to occur with the same ease, there is a very sharp increase in the content of functional groups for chemisorption of Ba(OH)<sub>2</sub>, which can be explained by the formation of acid anhydrides in the process of dehydration preceding decarboxylation, with the formation of anhydrides acids such as phthalic, which participate in the determination of total acidity with barium hydroxide, but do not participate in the reaction with calcium acetate when determining carboxyl groups. The relative ease of dehydration favors intramolecular anhydrides.



In addition, the decarboxylation process is facilitated by the presence of alkyl substituents, but the latter is partially eliminated during mechanochemical destruction and, in this case, decarboxylation is much more difficult. The OH-groups in these humic acids are also relatively unstable thermally; most of them decompose at a temperature of up to 300 °C. The high value of groups determined with Ba(OH)<sub>2</sub> in the products of thermal decomposition at 300 °C of dispersed humic acids is obvious due to acid anhydrides decarboxylating at higher temperatures. A significant part of the OH groups is confined to aromatic rings associated with the peripheral part of the molecules, and only a slightly larger amount compared to the humic acids of the Ekibastuz coal is confined to condensed aromatic rings.

As for the humic acids of the Kyzyl-Kiya wind-blown brown coal, it is obvious that the carboxyl groups in them are associated predominantly with the aromatic ring, which can be assumed based on the high degree of weathering, as a result of which such structural elements as aliphatic side chains and hydroaromatic rings are most susceptible to destruction. A certain number of carboxyl groups here are in opposition relative to the OH-groups, while carboxyl groups located nearby in one aromatic ring predominate, which are more difficult to remove than in the humic acids of the Karazhyra coal, due to the absence of alkyl substituents. The data obtained are consistent with the IR spectra results. These humic acids contain a small amount of thermally unstable OH-groups that decompose up to 200 °C and are not associated with a condensed aromatic ring.

The idea that under the influence of hydrodynamic forces, intermolecular bonds, in particular hydrogen ones, are weakened and partially broken, is also confirmed by the example of humic acids from the Karazhyra coal. In samples treated in the apparatus, aliphatic side chains and other weakened groups are eliminated at a lower temperature (300–400 °C), and at a higher temperature, due to the ordering of the structure, the weight loss is 1.6–4.3% lower compared with the original humic acids (Table 4).

A different dependence is observed for the humic acids of the Kyzyl-Kiya coal, where the initial sample at temperatures of 200 and 300 °C has a higher weight loss than the humic acids of treated coal, and in the temperature range 400–800 °C, the first, on the contrary, have slightly lower weight loss. In the humic acids of the Kyzyl-Kiya coal, under the influence of hydrodynamic forces, humic acids were formed from the relatively low molecular weight part of the insoluble residue, which is more easily exposed to high temperatures. The humic acids of the original and the Ekibastuz coal treated in the apparatus have very similar values.

Of the samples studied, weight loss at temperatures up to 300–400 °C is higher for the humic acids of the Kyzyl-Kiya coal, at temperatures of 400–800 °C it is the same as for the acids of the Ekibastuz coal.

When studying alkali-insoluble residues after extraction of humic acids, attention is drawn to the increase in ash content in samples subjected to hydrodynamic forces. Obviously, this occurs due to the

**Table 4.** Dependence of the weight loss of the humic acids of the original coals and those treated in a hydrodynamic rotor-pulsation apparatus on the heating temperature

Heating temperature, T °C	Weight loss by humic acids of coals, %					
	Karazhyra		Ekibastuz		Kyzylkiya	
	Original	Treated	Original	Treated	Original	Treated
100	1.25	1.60	1.25	1.40	1.40	1.60
200	8.8	10.8	10.0	9.7	11.2	10.6
300	16.0	17.1	17.2	17.5	19.6	18.1
400	27.2	25.6	29.0	29.0	27.6	29.5
500	37.8	33.8	40.0	39.9	35.3	38.3
600	43.8	39.5	44.8	45.0	41.6	44.5
700	47.2	44.5	48.5	48.1	46.2	47.6
800	49.8	46.2	50.3	50.4	49.0	50.8



**Table 5.** Changes in the chemical characteristics of the insoluble coal residue under the influence of hydrodynamic forces

Insoluble coal residues	Moisture, %	Ash, %	Elemental composition, % of organic mass			Content of functional groups mEq/g		3.98 Content of oxygen, %		C/H atomic
			C	H	O+I+S	COOH	OH	In functional	In an unaccounted	
Karazhyra original	9.2	24.8	72.27	9.08	18.65	0.00	2.90	4.64	14.01	0.663
Karazhyra treated	9.6	29.8	65.96	7.18	26.86	0.00	1.07	1.71	25.15	0.766
Ekibastuz original	5.2	24.5	68.70	7.93	23.37	0.02	0.73	1.23	22.14	0.722
Ekibastuz treated	5.0	30.5	66.26	8.39	25.35	0.02	1.73	1.23	22.52	0.658
Kyzylkiya original	10.6	34.9	62.61	3.77	33.621	0.01	2.44	2.83	29.63	1.384
Kyzylkiya treated	10.0	38.9	74.79	5.54	19.67	0.01	2.35	3.94	15.78	1.125

transition of part of the organic matter into a soluble state and due to the destruction of some complexes of humic acids, the ash part of which in the form of hydroxides remains in an insoluble residue (Table 5). From the elemental composition, we can see a decrease in the carbon of insoluble residues of the Karazhyra and Ekibastuz coals, with an increase in the atomic ratio of C/H and oxygen in an unaccounted form for the second and a decrease in C/H with a constant content of oxygen in an unaccounted form for the second.

The carbon content in the insoluble residue of the Kyzyl-Kiya coal increases significantly with a noticeable decrease in the atomic C/H ratio and oxygen in an unaccounted form. The content of functional groups of the insoluble residue of the Kyzyl-Kiya coal changes, in the Karazhyra coal it decreases by 2.7 times, and in the Ekibastuz coal it more than doubles due to the formation of OH-groups.

#### 4. Conclusions

From the data obtained, it can be concluded that under the influence of hydrodynamic forces, humic acid molecules are destroyed along the weakest bonds, oxygen-containing heterocycles, followed by hydrolysis, the transition of structures with a low degree of condensation into a soluble state and enrichment due to this insoluble residue with more condensed structures with a high hydrogen content in the Kyzyl-Kiya coal, constant oxygen content in an unaccounted form in the insoluble residue of the Ekibastuz coal and its increase in the insoluble residue of the Karazhyra coal is possible due to an increase in oxygen-containing groups (carbonyl and quinoid) formed during the mechanochemical de-

struction of coals. The possibility of increasing the degree of condensation of molecules due to the interaction of free radicals formed during the treatment cannot be excluded [39–41].

Thus, when hydrodynamic forces are applied to coals, along with the usually occurring increase in polydispersity and activation of the process of interaction of alkali with humic acids, destructive changes in molecules also occur, which have a different nature depending on the characteristics of the original coals' chemical structure. This is of great importance when developing technology for producing humates from coals and waste from lignite briquette factories.

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#### References

- [1]. Author's certificate 483142 USSR. Class B 03 d 1/14. Rotary apparatus. A.A. Bershtitsky, S.P. Tulchinsky. – B.I., 1975, No. 33.
- [2]. B.T. Omarov, Sh.M. Moldabekov, K.T. Zhantasov, Zh.M. Altybayev, et al. Influence of coal humic fertilizers on development of agriculture. *Reports of the National Academy of Sciences of the Republic of Kazakhstan* 2 (2016) 96–99. <http://reports-science.kz/images/pdf/d20162/d96-99.pdf>
- [3]. T.Zh. Umarov, O.I. Pobedonostseva, N.I. Pobedonostseva. Intensification of the process of coal oxidation under the influence of hydrodynamic forces. *Solid Fuel Chemistry* [Himija tverdogo top-liva] 4 (1981) 42–46. (in Russ.)

- [4]. I.I. Lishtvan, Yu.G. Yanuta, A.M. Abramets, V.P. Strigutskii, Yu.Yu. Navosha, *Solid Fuel Chem.* 47 (2013) 147–152. DOI: [10.3103/s0361521913030026](https://doi.org/10.3103/s0361521913030026)
- [5]. J. Dugarjav, B. Avid, S. Zherebtsov. Study of humic acids and preparations based on them. Book of Abstracts Fifth International Conference of CIS IHSS on Humic Innovative Technologies «Humic substances and living systems». October 19–23, 2019. DOI: [10.36291/hit.2019.dugarjav.109](https://doi.org/10.36291/hit.2019.dugarjav.109)
- [6]. S.I. Zherebtsov, K.S. Votolin, N.V. Malysenko, O.V. Smotrina, et al., *Solid Fuel Chem.* 53 (2019) 253–261. DOI: [10.3103/s0361521919050124](https://doi.org/10.3103/s0361521919050124)
- [7]. V.A. Kholodov, N.V. Yaroslavtseva, A.I. Konstantinov, I.V. Perminova, *Eurasian Soil Sci.* 48 (2015) 1101–1109. DOI: [10.1134/s1064229315100051](https://doi.org/10.1134/s1064229315100051)
- [8]. O.V. Rybachuk, M.P. Sartakov, V.A. Chumak, Electronic absorption spectra of hematomelanin and humic acids of peats of the Khanty-Mansiysk Autonomous District. *Eurasian Union of Scientists [Evrazijskij Sojuz Uchenyh (ESU)]* 7 (2014) 146–147. (in Russ.)
- [9]. B.T. Yermagambet, B.K. Kasenov, M.K. Kazankapova, Zh.M. Kassenova, et al., *Solid Fuel Chem.* 55 (2021) 41–46. DOI: [10.3103/s036152192101002x](https://doi.org/10.3103/s036152192101002x)
- [10]. M.M. Gertsen, E.D. Dmitrieva, O.S. Yanichkina, S.V. Ivanov. Directed chemical novolac-type modification of humic acids of peats. *Bulletin of Tver State University. Series: Chemistry* 4 (2019) 156–164. (in Russ.) [https://elibrary.ru/download/elibrary\\_41669150\\_41459023.pdf](https://elibrary.ru/download/elibrary_41669150_41459023.pdf)
- [11]. E.V. Maltseva, A.V. Savel'eva, A.A. Ivanov, N.V. Yudina, O.I. Lomovski, *Russ. J. Appl. Chem.* 87 (2014) 1070–1076. DOI: [10.1134/s1070427214080114](https://doi.org/10.1134/s1070427214080114)
- [12]. U. Nazarbek, S. Nazarbekova, Y. Raiymbekov, M. Kambatyrov, P. Abdurazova, *e-Polymers* 23 (2023). DOI: [10.1515/epoly-2023-0013](https://doi.org/10.1515/epoly-2023-0013)
- [13]. U. Nazarbek, P. Abdurazova, S. Nazarbekova, D. Assylbekova, et al., *Appl. Sci.* 12 (2022) 3658. DOI: [10.3390/app12073658](https://doi.org/10.3390/app12073658)
- [14]. S.N. Chukov. The concept of evolutionary humification. Book of Abstracts Seventh International Conference on Humic Innovative Technologies “Humic substances and technologies for resilience”, November 18–21, 2022. DOI: [10.36291/hit.2022.083](https://doi.org/10.36291/hit.2022.083)
- [15]. M.U. Isokov, R.S. Alimov, I.M. Almatov, S.A. Soatov, *Obogashchenie Rud* 5 (2022). DOI: [10.17580/or.2022.05.07](https://doi.org/10.17580/or.2022.05.07)
- [16]. H.R. Schulten. Chapter 3. Models of Humic Structures: Association of Humic Acids and Organic Matter in Soils and Water. In.: Humic Substances and Chemical Contaminants, 2001. DOI: [10.2136/2001.humicsubstances.c4](https://doi.org/10.2136/2001.humicsubstances.c4)
- [17]. J. Smilek, P. Sedláček, M. Kalina. The interactions of organic species with humic acids studied by dialysis techniques. Comparison of selectively methylated with “natural” humic acids. Book of Abstracts Fifth International Conference of CIS IHSS on Humic Innovative Technologies «Humic substances and living systems». October 19–23, 2019. DOI: [10.36291/hit.2019.smilek.046](https://doi.org/10.36291/hit.2019.smilek.046)
- [18]. R. Baigorri, J. Erro, Ó. Urrutia, J.M. Martinez, M. Mandado, M. Martín-Pastor, et al., *RSC Adv.* 9 (2019) 25790–25796. DOI: [10.1039/c9ra04383g](https://doi.org/10.1039/c9ra04383g)
- [19]. K.T. Arynov, A.P. Auyeshov, M.F. Faskhutdinov, O.T. Zhilkibayev. Increase of efficiency of liquid humic fertilizers based on the use of combined feedstock. Book of Abstracts Fifth International Conference of CIS IHSS on Humic Innovative Technologies «Humic substances and living systems», October 19–23, 2019. DOI: [10.36291/hit.2019.arynov.103](https://doi.org/10.36291/hit.2019.arynov.103)
- [20]. E. Tombácz, J.A. Rice. CHANGES OF COLLOIDAL STATE IN AQUEOUS SYSTEMS OF HUMIC ACIDS. Understanding Humic Substances. 1999, p. 69–78. DOI: [10.1016/b978-1-85573-815-7.50012-x](https://doi.org/10.1016/b978-1-85573-815-7.50012-x)
- [21]. N.U. Mulloev, N.A. Lutfiloev, S. Odinaev, M.I. Dergacheva, N.L. Lavrik. Comparative analysis of the spectral characteristics of humic acids of various genesis. *Proceedings of the Academy of Sciences of the Republic of Tajikistan* 63 (2020) 78–84 (in Russ.) [https://elibrary.ru/download/elibrary\\_43863769\\_61447274.pdf](https://elibrary.ru/download/elibrary_43863769_61447274.pdf)
- [22]. A.V. Savel'eva, N.V. Yudina, E.M. Berezina, E.V. Petrova, *Solid Fuel Chem.* 50 (2016) 76–80. DOI: [10.3103/s0361521916020105](https://doi.org/10.3103/s0361521916020105)
- [23]. V.D. Tikhova, T.F. Bogdanova, V.P. Fadeeva, V.N. Piottukh-Peletsky, *J. Anal. Chem.* 68 (2013) 86–94. DOI: [10.1134/s1061934813010139](https://doi.org/10.1134/s1061934813010139)
- [24]. K.S. Votolin, S.I. Zherebtsov, O.V. Smotrina, Z.R. Ismagilov, *Chemistry for Sustainable Development* 6 (2019) 576–583. DOI: [10.15372/csd2019176](https://doi.org/10.15372/csd2019176)
- [25]. A.V. Savel'eva, A.A. Ivanov, N.V. Yudina, O.I. Lomovsky, Dzh. Dugarzhav, *Russ. J. Appl. Chem.* 86 (2013) 552–557. DOI: [10.1134/s1070427213040174](https://doi.org/10.1134/s1070427213040174)
- [26]. N.V. Yudina, A.V. Savel'eva, E.V. Linkevich, *Solid Fuel Chem.* 53 (2019) 29–35. DOI: [10.3103/s0361521919010099](https://doi.org/10.3103/s0361521919010099)
- [27]. I.M. Nikitina, S.A. Epshtein, N.A. Fomenko, E.L. Kossovich, *Eurasian Mining* 2 (2016) 33–36. [https://rudmet.net/media/articles/Article\\_EM\\_02\\_16\\_pp.33-36\\_1.pdf](https://rudmet.net/media/articles/Article_EM_02_16_pp.33-36_1.pdf)
- [28]. A.V. Savel'eva, N.V. Yudina, *Solid Fuel Chem.* 48 (2014) 328–331. DOI: [10.3103/s0361521914050127](https://doi.org/10.3103/s0361521914050127)

- [29]. M.B. Amangulyev, The main quantities characterizing the chemical activity of humic acids. *Symbol of Science: International Scientific Journal* 9-1 (2023) 11–12.
- [30]. V.A. Avramenko, S.Yu. Bratskaya, A.S. Yakushevich, A.V. Voit, et al. *Geochem. Int.* 50 (2012) 437–446. DOI: [10.1134/s0016702912030032](https://doi.org/10.1134/s0016702912030032)
- [31]. T.S. Skripkina, L.I. Yudina, V.D. Tikhova, A.L. Bychkov, I.O. Lomovsky, *Solid Fuel Chem.* 57 (2023) 402–410. DOI: [10.3103/s0361521923060071](https://doi.org/10.3103/s0361521923060071)
- [32]. A.V. Savel'eva, A.A. Ivanov, N.V. Yudina, O.I. Lomovskii, *Solid Fuel Chem.* 49 (2015) 201–205. DOI: [10.3103/s0361521915040096](https://doi.org/10.3103/s0361521915040096)
- [33]. A.G. Proidakov, *Solid Fuel Chem.* 43 (2009) 9–14. DOI: [10.3103/s0361521909010030](https://doi.org/10.3103/s0361521909010030)
- [34]. I.I. Lishtvan, V.P. Strigutskii, Yu.G. Yanuta, A.M. Abramets, et al., *Solid Fuel Chem.* 46 (2012) 153–158. DOI: [10.3103/s036152191203007x](https://doi.org/10.3103/s036152191203007x)
- [35]. T.S. Urazova, A.L. Bychkov, O.I. Lomovskii, *Russ. J. Appl. Chem.* 87 (2014) 651–655. DOI: [10.1134/s1070427214050206](https://doi.org/10.1134/s1070427214050206)
- [36]. R.P. Koroleva, Sh.Zh. Zhorobekova, E.D. Kasymova, K.A. Kydralieva. Donor-acceptor properties of humic acids. *News of the National Academy of Sciences of the Kyrgyz Republic* 2 (2013) 36–41.
- [37]. M.A. Promptov, A.Yu. Stepanov, *Vestnik Tambovskogo gosudarstvennogo tehnikeskogo universiteta* 27 (2021) 263–274. (in Russ.) DOI: [10.17277/vestnik.2021.02.pp.263-274](https://doi.org/10.17277/vestnik.2021.02.pp.263-274)
- [38]. T. Skripkina, A. Ulihin, A. Bychkov, S. Mamylov, et al., *RSC Adv.* 10 (2020) 21108–21114. DOI: [10.1039/d0ra03131c](https://doi.org/10.1039/d0ra03131c)
- [39]. S.L. Khil'ko, I.V. Efimova, O.V. Smirnova, *Solid Fuel Chem.* 45 (2011) 367–371. DOI: [10.3103/s036152191106005x](https://doi.org/10.3103/s036152191106005x)
- [40]. G.D. Chimitdorzhieva, D.B. Andreeva, V.M. Korsunov, *Dokl. Biochem. Biophys.* 384 (2002) 189–192. DOI: [10.1023/a:1016040718493](https://doi.org/10.1023/a:1016040718493)
- [41]. I.I. Lishtvan, V.P. Strigutskii, Yu.G. Yanuta, A.M. Abramets, et al., *Solid Fuel Chem.* 51 (2017) 301–307. DOI: [10.3103/s036152191705010x](https://doi.org/10.3103/s036152191705010x)