МРНТИ 52.35.01 https://doi.org/10.18321/cpc23(3)345-357

Synthesis and Properties of Humic Acids Derived from Brown coal of Kuznetsk and Kumuskuduk Deposits

A.P. Nauanova[1], T.O. Khamitova[1*], N. Parmanbek[2*], S. Tyanakh[3*], R.Z. Kasenov[3], S.Zh. Davrenbekov[3], A.N. Bolatbay[3], U.B. Toleuov[3]

[1]S. Seifullin Kazakh Agro Technical Research University, Zhenis ave., 62, Astana, Kazakhstan
[2]The Institute of Nuclear Physics, Ibragimov st., 1, Almaty, Kazakhstan
[3]E.A. Buketov Karaganda University, University st., 28, Karaganda, Kazakhstan

ARTICLE INFO:

Received
16.03.2025

Received in revised form
18.04.2025

Accepted
29.08.2025

Keywords:
brown coal; humic acids; Kumuskuduk deposit; Kuznetsk deposit; functional groups; infrared spectroscopy; elemental analysis; ash content; reactivity

ABSTRACT

This article presents the synthesis and comparative characterization of humic acids extracted from brown coal deposits of Kuznetsk and Kumuskuduk in Kazakhstan. Advanced analytical techniques, including infrared (IR) spectroscopy, elemental analysis, and thermogravimetric/differential scanning calorimetry (TGA/DSC), were employed to investigate the physicochemical and structural properties of the humic acids derived from these two distinct geological sources. The results revealed significant differences in elemental composition, particularly in carbon, oxygen, and hydrogen content, which were directly related to the geological and environmental conditions under which the coals were formed. Variations in the concentration of carboxyl and hydroxyl functional groups were also identified, influencing the sorption capacity, acidity, and complexation behavior of the humic acids. Thermal analysis demonstrated differing levels of thermal stability and decomposition patterns, reflecting the structural heterogeneity of the samples. This study highlights the importance of geological origin in determining the functional potential of humic substances and supports their application in environmental remediation, agriculture, and water purification.

1. Introduction

Kazakhstan ranks among the top ten coal-producing countries in the world, with large deposits of lignite and sub-bituminous coals, especially in regions like Karaganda, Ekibastuz, and the Kumuskuduk fields. These deposits are rich in organic matter, making them ideal for the extraction of humic acids.

The country's vast reserves offer a reliable, cost-effective source of raw material for producing humic substances, positioning Kazakhstan to meet both domestic and international demand. Humic substances are known for their ability to improve soil quality, increase water retention, and remediate polluted soils by binding heavy metals and organic contaminants. Kazakhstan, with its history of industrial activity and mining, faces significant environmental challenges, including soil and water contamination. The extraction and application of humic substances from domestic coal sources offer a promising solution for mitigating environmental degradation, thus stimulating the market for these materials [1-3].

The market for humic substances derived from coals in Kazakhstan is on an upward trajectory, driven by the country's abundant coal resources and the growing demand for sustainable agricultural and environmental solutions. With continued investment and government support, Kazakhstan is well-positioned to expand its production and export capacity, making humic substances a key contributor to its green economy and environmental initiatives [4]. Humic acids (HAs) are essential components of natural organic matter, widely distributed in soils, sediments, and water bodies. These complex, heterogeneous macromolecules are formed by the decomposition of plant and animal material over time and play a crucial role in various environmental and biological processes. Humic acids possess unique physicochemical properties, including the ability to chelate metal ions, adsorb organic pollutants,

Corresponding author: S. Tyanakh *E-mail address: saika_8989@mail.ru

and enhance soil structure. As a result, they are extensively studied for their potential applications in agriculture, environmental remediation, and industry. Despite the significant interest in humic substances, their properties are influenced by their origin and the conditions under which they are formed, necessitating further research on humic acids derived from different natural sources [5, 6].

Brown coal, or lignite, represents a promising raw material for the extraction of humic acids due to its high organic content and relatively low degree of carbonization. The Kuznetsk Basin in the central region of Kazakhstan and the Kumuskuduk region are two significant deposits of brown coal with differing geological and environmental characteristics. While these deposits are abundant, the properties of humic acids synthesized from their brown coal remain insufficiently explored. Understanding the relationship between the source material and the properties of the resulting humic acids is critical for optimizing their use in various practical applications [7, 8].

This study focuses on the synthesis of humic acids from brown coal extracted from the Kuznetsk and Kumuskuduk deposits, with the objective of analyzing and comparing their physicochemical properties. Through detailed characterization, including elemental analysis, functional group identification, and molecular weight distribution, this research aims to elucidate the factors that influence the performance of humic acids derived from these distinct coal sources. The findings of this work are expected to contribute to the development of more efficient humic acid-based products and technologies in agriculture, environmental management, and industrial processes, while also advancing the fundamental understanding of humic substances from different coal deposits [9, 10].

2. Materials and methods

The physico-chemical characteristics of lignite from different deposits can exhibit substantial variability due to the geological conditions under which it formed, as well as the composition of its organic and mineral constituents. Essential parameters for evaluating lignite's suitability for diverse applications – such as energy production, chemical processing, and environmental protection – include moisture content, ash content, volatile matter yield, and the types of functional groups present.

In this study, lignite samples from the Kumuskudyk and Kuznetsk deposits were examined. These samples represent coal resources with specific physicochemical properties, making them valuable for investigating the extraction of humic acids and assessing their potential applications in fields like agriculture and environmental management. Analyzing these samples provides deeper insights into lignite's composition and structure, along with its reactivity with various agents in the process of humic substance extraction.

The Kumuskudyk coal mine, one of Kazakhstan's largest coal-producing sites, is operated by the joint-stock company «Sat Komir Mining Company» This mine, located in the Bukar Zhyrau district of the Karaganda region approximately 35 km east of Karaganda, primarily produces B-3 lignite. Similarly, the Kuznetsk coal mine, an important coal operation in Kazakhstan under the Kuznetsk company, is situated in the same district and approximately the same distance from Karaganda. The Kuznetsk mine is one of the top ten coal producers in Kazakhstan and is also known for its output of B-3 lignite.

In the initial phase of the study, lignite samples from the Kumuskudyk (KUM) and Kuznetsk (KUZ) deposits were selected as raw materials for humic acid extraction. To enhance surface area and improve the efficiency of humic acid extraction, each sample was pre-ground to a particle size of 0.5-1 mm using a «Vibrotechnik ShKD-6» crusher. Subsequently, the coal samples were dried in an oven at 80 °C for 8 h to eliminate moisture.

Extraction of humic acid from coal using the hydro-alkaline method. Humic acids were extracted from lignite using an aqueous-alkaline method, which involves the precipitation of humic acids in an acidic medium facilitated by sodium hydroxide (NaOH). This method isolates humic acids through their reaction with NaOH, followed by separation via precipitation, as described by the following equation.

Humic acids were extracted from the coal samples by adding NaOH, followed by precipitation using an acidic reagent. During the extraction, 10.0-20.0 g of coal was accurately weighed to 0.0001 g and placed in a 250 cm^3 flask. In the next stage, 100 cm^3 of a 4% sodium hydroxide solution was added. The mixture was heated to 80 °C and stirred on a shaker for 2 h. The resulting suspension was filtered or centrifuged to remove undissolved carbon residues, which were subsequently rinsed with a small amount of alkaline solution. The remaining solid carbon was dried and weighed for further analysis. The volume of the filtered solution was recorded, and the humic acid content in the final product was determined.

$$\begin{aligned}&\text{Coal} + \text{NaOH HA} - \text{COONa} + \text{HMA} - \text{COONa} + \text{FA} - \text{COONa},\\&2\ \text{HA} - \text{COONa} + 2\ \text{HMA} - \text{COONa} + 2\ \text{FA} - \text{COONa} + 3\ \text{HCl},\\&2\ \text{HA} - \text{COONa} + 2\ \text{HMA} - \text{COONa} + 2\ \text{FA} - \text{COONa} + 3\ \text{NaCl}\end{aligned} \tag{1}$$

Humic acid was precipitated by adjusting the pH of the solution to 2-3 using a 5% HCl solution. The mixture was then allowed to settle for 60 min after which the humic acid precipitate was collected on a pre-weighed (blue-strip) filter paper. The precipitate was thoroughly rinsed with distilled water to remove any impurities and residual reagents. Following filtration, the filter paper with the precipitate was carefully removed from the Buchner funnel, folded, and pre-dried. It was then placed in a pre-weighed beaker and dried in an oven at 80 °C until a constant weight was achieved, ensuring complete moisture removal and enabling accurate measurement of the humic acid mass obtained [11].

The chemical process outlined involves the transformation of coal into humic substances, specifically humic acid (HA), humic matter (HMA), and fulvic acid (FA), through a series of reactions with sodium hydroxide (NaOH) and hydrochloric acid (HCl). These transformations are typical in the context of coal humification processes and may have significant implications for the formation of useful humic substances in environmental and industrial applications.

The elemental composition of the samples. The elemental composition of the samples was analyzed using a CHNS-O UNICUBE organic elemental analyzer from Elementar Analysensysteme GmbH (Germany). This analysis was carried out in the laboratory of Nazarbayev University. The analyzer operates on the classic Dumas-Pregl method, which involves combustion of the samples in the presence of an oxidizing agent within an inert gas stream. During the combustion process, oxygen was supplied continuously, leading to the formation of analytical gases such as carbon dioxide (CO_2), water (H_2O), molecular nitrogen (N_2), and sulfur dioxide (SO_2). To ensure precise sample weighing, a Mettler Toledo XPR6U Ultra-Microbalance was investigated. Samples were placed in disposable tin boats with a thickness of less than 0.01 mm and sealed with tweezers to prevent sample loss.

Weight range: suitable for use from micro quantities (<1 mg) to macro quantities (approximately 1 g), with a maximum of 15 mg of organic matter. Element concentration ranges are as follows:

– Carbon (C): up to 14 mg absolute or 0-100% (up to 50 mg in CN mode*);

– Hydrogen (H): up to 2 mg absolute or 0-100%;

– Nitrogen (N): up to 10 mg absolute or 0-100%;

– Sulfur (S): up to 3 mg absolute or 0-100%;

– Oxygen (O*): up to 6 mg absolute or 0-100%.

Accuracy: less than 0.1% absolute composition (for a homogeneous substance), depending on sample type, analysis mode, and configuration. Sample combustion was conducted in a quartz reactor within ELEMENTAR's Unicube analyzer, equipped with a high-temperature-resistant ceramic lining, enabling combustion at temperatures up to 1150 °C without the use of catalysts. The oxidation column was maintained at 1150 °C, while the reduction column was set to 850 °C. Each sample was analyzed in triplicate, and the results were averaged for accuracy. Calibration and verification of the equipment were performed using a sulfonamide standard from Elementar Analysensysteme GmbH. Tin boats with dimensions of 4×4×11 mm and high-purity gases, helium (99.9999%) and oxygen (99.999%), were used in the measurements. The base standard applied was ASTM D5373, which specifies test methods for determining carbon, hydrogen, and nitrogen in coal samples, as well as carbon in coal and coke samples, using combustion analysis techniques [12].

3. Results and discussions

Analysis of the elemental composition of samples. The carbon (C), hydrogen (H), nitrogen (N), sulfur (S), and oxygen (O) content in various samples was determined using a CHNS-O UNICUBE elemental analyzer from Elementar Analysensysteme GmbH. The analysis provided average values for the content of oxygen (O), carbon (C), hydrogen (H), nitrogen (N), and sulfur (S) in brown coal from the Kuznetsk open-pit mine (sample KUZ-2024) and in the ash produced after its combustion (sample Zola KUZ-2024). The results are presented in Table 1.

Brown coal from the Kuznetsk open-pit mine is notable for its high carbon content (56.02%), indicating a substantial calorific value and suitability as a fuel source. The elevated oxygen (25.07%) and hydrogen (5.085%) levels suggest a significant amount of volatile compounds, contributing to high reactivity and enhanced combustion efficiency. The absence of nitrogen minimizes the risk of nitrogen oxide (NO_x) formation, which is beneficial for its environmental impact. Additionally, the low sulfur content (0.155%) implies a reduced likelihood of sulfur dioxide (SO_2) emissions, though monitoring SO_2 emissions during combustion remains essential to mitigate air pollution.

The ash sample exhibits a marked reduction in oxygen (to 11.56%), carbon (to 12.33%), and hydrogen (to 0.16%) content compared to the original coal, indicating that a substantial portion of oxygen and hydrogen was released as combustion gases, such as carbon dioxide (CO_2) and water vapor (H_2O). The presence of 12.33% carbon in the ash suggests residual organic material, which could support the use of ash as a component in organomineral fertilizers. The nitrogen content of 0.43% in the ash is likely due to the formation of nitrogen compounds (NO_x) during coal combustion in an air atmosphere.

The reduction in oxygen and carbon content following combustion results from the transformation of these elements into gaseous combustion products. The remaining carbon content in the ash at 12.33% reflects incomplete oxidation, which could allow for the potential reuse of the ash. Hydrogen, initially at 5.085% in the coal, is nearly absent (0.16%) in the ash due to its release as water vapor. Sulfur, initially present at 0.155% in the coal, is entirely absent in the ash, suggesting it volatilized during combustion as gaseous compounds, such as sulfur dioxide (SO_2).

The ash produced from the combustion of brown coal shows potential as a component in organomineral soil ameliorants. The residual carbon and nitrogen content may contribute to enhancing soil fertility and improving soil structure. The absence of sulfur in the ash is advantageous from an environmental perspective, as excessive sulfur content could result in soil acidification. The low hydrogen and oxygen levels in the ash further indicate its predominantly mineral nature, which can positively influence the soil's physical and chemical properties.

In conclusion, the ash derived from brown coal of the Kuznetsk open-pit mine has potential for use in soil improvement. However, further analysis is required to assess the presence of heavy metals and toxic elements to provide a comprehensive evaluation of its suitability for this purpose [13].

The elemental analysis of brown coal from the Kumuskuduk open-pit mine revealed that its primary components are carbon (C), oxygen (O), hydrogen (H), nitrogen (N), and sulfur (S). According to the data in Table 1, the average carbon content in these samples was 50.855%, reflecting typical characteristics of low-grade brown coal from this region. This level of carbon suggests a relatively high calorific value, as carbon is the primary energy source in fuel combustion. However, the notable oxygen content (25.07%) indicates a high level of moisture and oxygenated compounds, which diminishes the coal's energy efficiency. The results are presented in Table 2.

The hydrogen content in the sample is 5.294%, which significantly contributes to the calorific value, as hydrogen releases substantial energy upon combustion. Therefore, its presence enhances the fuel's energy potential. The nitrogen content was found to be 0.455%, which is relatively low. This is beneficial for the coal's environmental performance, as higher nitrogen levels can lead to nitrogen oxide (NO_x) emissions during combustion, a source of atmospheric pollution. Additionally, the sulfur content in Kumuskuduk brown coal is 0.138%, which is also low. This low sulfur level makes the coal environmentally preferable, as it minimizes sulfur oxide (SO_x) emissions, reducing the potential for acid rain formation during combustion.

Analysis of the coal ash revealed a notable reduction in carbon content to 11.14%, indicating that a substantial portion of the organic matter

Table 1. Average Content of Oxygen (O), Carbon (C), Hydrogen (H), Nitrogen (N), and Sulfur (S) in Brown Coal from the Kuznetsk Open-Pit Mine and in the Ash Resulting from Its Combustion

№	Name	Oxygen (O), %	Carbon (C), %	Hydrogen (H), %	Nitrogen (N), %	Sulfur (S), %
1	Kuz-2024	25.07	56.02	5.085	0	0.155
2	Zola Kuz-2024	11.56	12.33	0.16	0.43	0

Table 2. Average content of oxygen (O), carbon (C), hydrogen (H), nitrogen (N), and sulfur (S) in brown coal from the Kumuskuduk open-pit mine and in the ash produced after its combustion

№	Name	Oxygen (O), %	Carbon (C), %	Hydrogen (H), %	Nitrogen (N), %	Sulfur (S), %
1	Kuz-2024	25.07	50.855	5.294	0.455	0.138
2	Zola Kuz-2024	11.56	11.14	0.136	0.36	0

was consumed during combustion. Additionally, the minimal levels of hydrogen and sulfur in the ash further confirm their extensive burnout during the combustion process.

The analysis of the elemental composition of brown coal from the Kumuskuduk deposit leads to the following conclusions:

– The coal has a high carbon content (approximately 51%), suggesting a substantial calorific value. However, a relatively high oxygen content (25%) implies significant moisture, potentially reducing the efficiency of its energy use;

– The low sulfur (0.138%) and nitrogen (0.455%) levels contribute to its environmentally friendly profile, resulting in minimal pollutant emissions during combustion;

– The hydrogen content of 5.294% enhances the coal's calorific value, though moisture and oxygen remain key factors impacting its energy potential;

– Coal ash analysis confirmed an efficient combustion process, evidenced by a high degree of organic burnout and minimal residual elements, such as carbon, hydrogen, and sulfur.

In summary, brown coal from the Kumuskuduk mine shows promise as a fuel source for the energy sector, particularly due to its low sulfur and nitrogen content, which helps to minimize its environmental impact [14].

The analysis of coal ash composition (sample Zola Kum-2024) suggests its potential for use as a component in organomineral ameliorants. Despite a reduction in carbon content from 50.855% in the original coal to 11.14% in the ash, the remaining carbon in the ash is still significant, indicating the preservation of organic material. This organic component can positively influence soil structure, enhance water retention, and promote the growth of soil microorganisms, which are crucial for improving soil fertility. The nitrogen content (0.36%) in the ash, although low, could contribute to the nitrogen balance of the soil, benefiting plant growth by providing a small but valuable source of this essential nutrient. The absence of sulfur in the ash is beneficial from an environmental perspective, as excessive sulfur content can lead to soil acidification, which harms soil fertility. Thus, the lack of sulfur makes the ash environmentally safe and suitable for use in soil amelioration.

The oxygen content (O) of 11.56% and hydrogen content (H) of 0.136% in the ash indicate the presence of oxidizing components, which may participate in reactions with other substances in the soil. However, these low values suggest that the ash will primarily function as a mineral component, enhancing the physical structure of the soil.

The analytical data for coal ash from the Kumuskuduk coal mine (Zola Kum-2024) suggest its potential as a source of organomineral ameliorants. The ash contains sufficient carbon to enhance soil structure and fertility. Additionally, its low sulfur and nitrogen content renders it suitable for agricultural applications. However, to comprehensively evaluate the ash's agricultural suitability, it is essential to assess the presence of heavy metals and other potentially toxic pollutants. The concentration of these elements could severely restrict the ash's applicability in agronomy and pose risks to both ecosystems and plant health.

Characterization of functional groups. The functional groups in the samples were identified using an FSM 1202 FTIR spectrometer. To prepare the samples, carbon was ground and mixed with potassium bromide (KBr) to form tablets. The spectra were acquired over a wavenumber range of 4000-400 cm^{-1} with a resolution of 4 cm^{-1}. The analysis primarily focused on the absorption bands corresponding to specific functional groups, including carboxyl (-COOH), hydroxyl (-OH), aromatic (C=C), as well as aliphatic hydrocarbon (C-H) groups. The results are illustrated in Fig. 1.

As illustrated in Fig. 1, the band in the 3800–3600 cm^{-1} region corresponds to water bound to the coal surface or hydroxyl groups formed during chemical reactions. In the 2000-1600 cm^{-1} range, absorption peaks related to C=O bond vibrations are observed, which can be attributed to carbonyl compounds such as ketones, aldehydes, or carboxyl groups. These bands in coal are likely due to oxygen-containing functional groups involved in oxidation processes. The band between 1600-1300 cm^{-1} is associated with the deformation vibrations of C-H and C=C bonds in aromatic rings. Given that coal contains numerous aromatic structures, this range can provide insights into the aromaticity of the carbon skeleton; stronger bands in this region suggest a higher content of aromatic carbons. The 1000-750 cm^{-1} region may indicate the presence of substituted benzene rings (aromatic hydrocarbons) and C-H in-plane vibrations, as well as vibrations of carbon–oxygen bonds in structures such as ethers or alcohols, if these functional groups are present.

Differential scanning calorimetry (TGA)/DSC analysis. Thermogravimetric (TG) and differential scanning calorimetry (DSC) analysis were conducted using a LABSYSTMEvoTG-DTA/DSC instrument (SETARAM, France) to evaluate the thermal stability

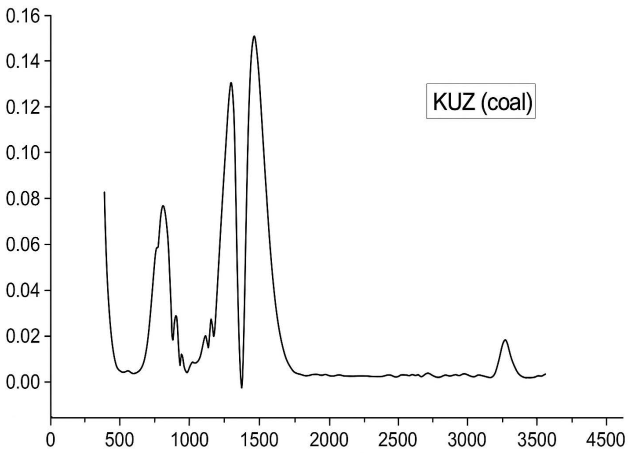

Fig. 1. IR spectrum of the sample.

of the samples and investigate their decomposition behavior upon heating. Coal samples were placed in aluminum oxide crucibles and subjected to a constant heating rate of 10 °C/min in an air atmosphere, reaching a maximum temperature of 800 °C. During the analysis, changes in sample mass were continuously recorded, allowing for the determination of the temperatures at which key stages of organic matter decomposition occur. This also facilitated the quantification of moisture, volatile matter, fixed carbon, and ash content. Additionally, TGA provided insights into the stability of the organic components of the coal and its potential reactivity. The results are illustrated in Fig. 2.

As shown in Fig. 2, the first phase of mass loss occurred between 100-150 °C, which is attributed to the evaporation of moisture. The second phase, occurring between 200-400 °C, is associated with the release of volatile substances, including low-molecular hydrocarbons and other organic compounds. The third phase, spanning 400-600 °C, corresponds to the decomposition of the primary organic matrix of coal, involving the breakdown of

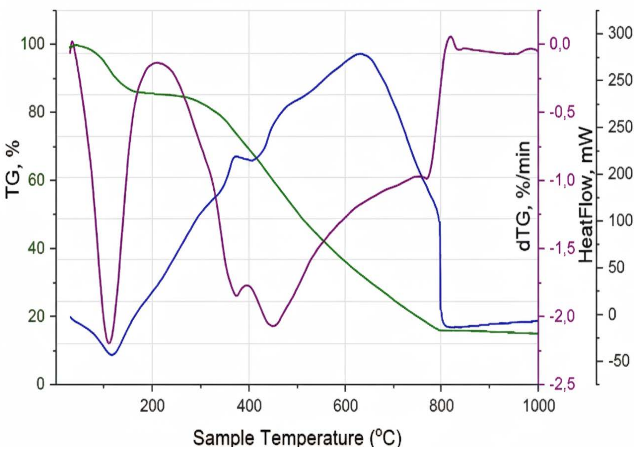

Fig. 2. Results of TG/DSC analysis of Kumuskuduk coal.

complex macromolecules such as humic substances and hydrocarbons. The remaining mass between 600-800 °C reflects the mineral content (ash), which was further corroborated by the ash residue observed following the TG analysis.

Characterization of pore sizes and volumes, moisture content, and density. In the course of the experiments, the ash and moisture content of coal samples from the Kumuskuduk (KUM) and Kuznetsk (KUZ) deposits were measured. The results of these analyses are presented in Table 3.

The results revealed that the ash content of coal from the Kumuskuduk deposit is 22%, with a moisture content of 8.24%. The volatile substance yield for this sample is 50.86%. In contrast, the coal from the Kuznetsk deposit exhibited a considerably lower ash content of 7.4% and a moisture content of 9.5%. The yield of volatile substances in the Kuznetsk coal samples ranges from 47% to 50%. These findings highlight significant differences in the characteristics of the coals from the two deposits, which could influence the selection of appropriate technologies for their processing and the extraction of humic substances.

Quantitative determination of humic substance yield from coal waste. The experiments resulted in the extraction of humic acids from coal samples of the Kumuskuduk deposit using the alkaline hydrolysis method. From 10 g of Kumuskuduk coal, 0.7 g of humic acids were obtained, corresponding to a yield of 7%.

In the optimization of humic acid extraction, various process parameters were examined, including alkali solution concentration (1-4%), temperature (20-80 °C), and reaction time (30-120 min). Experimental results indicated that the most efficient separation of sodium humates occurred with a 4% alkali solution at 80 °C for 120 min.

Higher alkali concentrations facilitated more complete extraction of humic acids, whereas increasing the temperature above 80 °C resulted in a reduction in sodium humate yield (from 4% to 2%) and significant changes in the product composition. This is attributed to the hydrolysis and leaching of carboxyl and polysaccharide fragments, which led to an increased relative content of aromatic structures (up to 44-45%).

Table 3. Ash and humidity content of the coal samples

Indicator	KUM	KUZ
Ash content, Aa, %	22	7.4
Humidity, Wa, %	8.24	9.5

Prolonging the reaction time beyond 2 h did not notably enhance the extraction of humic acids. Therefore, the optimal conditions for humic acid extraction were found to be a 4% alkali solution, 80 °C, and a reaction time of 120 min.

Spectroscopic analysis of humic substance content and investigation of structural characteristics. Humic acids were extracted from coal samples of the Kumuskuduk and Kuznetsk deposits through alkaline hydrolysis in the course of the experiments. The extracted humic acid samples were subsequently analyzed using infrared (IR) spectroscopy and thermogravimetric (TG)/differential scanning calorimetry (DSC) techniques. The results are illustrated in Fig. 3.

As shown in Fig. 3, the absorption band in the 3800-3550 cm^{-1} range corresponds to the vibrations of O-H groups, which are characteristic of hydroxyl groups found in both free water and hydrogen bonds within the structure of humic acids. The 2100-1600 cm^{-1} range displays absorption bands associated with carboxylic acids, aldehydes, ketones, and esters. The 1600-1250 cm^{-1} region is linked to the vibrations of aromatic C=C bonds, typical of humic acids, which contain aromatic rings in their structure. Deformation vibrations of C-O bonds in carboxylic and phenolic groups may also appear in this range, indicating the presence of complex oxygen-containing functional groups in humic acids. Between 1000-600 cm^{-1}, absorption bands are observed for deformation vibrations of C-H bonds in aromatic rings and C-O-C bond vibrations in esters and ether groups. The low-frequency range of 600-500 cm^{-1} corresponds to out-of-plane vibrations in aromatic systems and deformations of C-C bonds in carbon chains. Thermogravimetric analysis of the humic acids was conducted in an inert atmosphere up to a temperature of 1000 °C. The results are illustrated in Fig. 4.

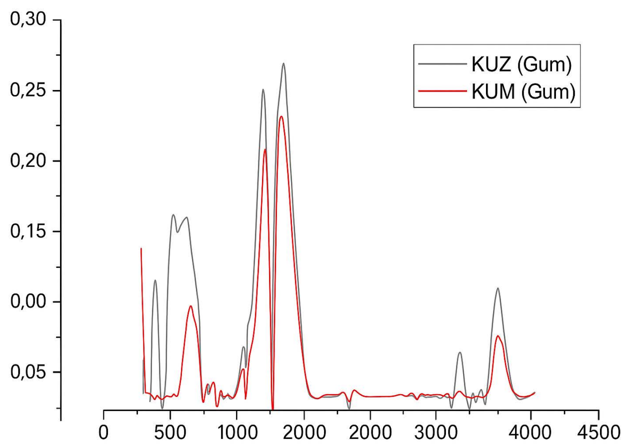

Fig. 3. Infrared (IR) spectra of the extracted humic acids.

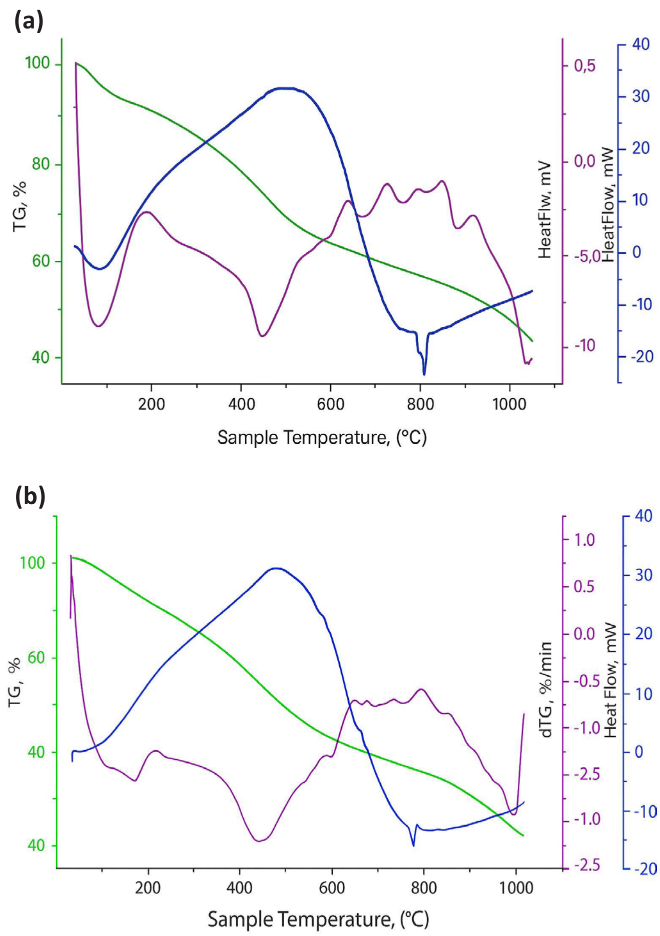

Fig. 4. Results of TG/DSC analysis of humic acid samples (a) – KUZ; (b) – KUM.

As observed from the thermogravimetric analysis curves of the humic acids, in the temperature range of 30-175 °C, there is only a minor mass change, likely due to the presence of residual water. The decomposition of the sample occurs in two main stages. The first stage, between 200-500 °C, is characterized by the breakdown of volatile substances and functional groups such as carboxyl, phenolic, and methoxyl groups. During this stage, small organic molecules associated with aromatic structures are also decomposed, leading to a significant mass loss. This stage involves the release of water, carbon dioxide, and other low-molecular-weight gases. The second stage, occurring between 550-1000 °C, involves the degradation of more stable aromatic structures and condensed polycyclic systems, resulting in further mass loss and the formation of carbon residues. This stage is associated with carbonization, where organic matter is converted into carbon, and the formation of a stable residue similar to coke. These stages illustrate the sequential thermal decomposition of humic acids, from the breakdown of lighter functional groups to the formation of stable carbon structures.

Table 4. Average content of oxygen (O), carbon (C), hydrogen (H), nitrogen (N), and sulfur (S) in humic acids

№	Name	Carbon (C), %	Hydrogen (H), %	Nitrogen (N), %	Sulfur (S), %	Oxygen (O), %
1	Humic acid (Kuznetsk)	49.605	3.071	0.93	0.391	45.263
2	Humic acid (Kumuskuduk)	46.69	3.079	0.63	0.172	48.26

Analysis of the chemical composition of the humic product. Subsequently, the elemental composition of carbon (C), hydrogen (H), nitrogen (N), sulfur (S), and oxygen (O) in humic acids (HA) extracted from the brown coals of the Kumuskuduk and Kuznetsk deposits was determined using the CHNS-O UNICUBE elemental analyzer (Elementar Analysensysteme GmbH). This analysis was conducted to assess the elemental composition of the humic acids, providing insights into their chemical properties and potential applications in agriculture.

Table 4 presents the average percentage values of chemical element content in humic acids derived from different deposits.

Humic acid from the Kuznetsk deposit shows a higher carbon content (49.605%) than that from the Kumuskuduk deposit (46.69%), suggesting a greater degree of aromaticity or polymerization in the organic material of Kuznetsk coals. Hydrogen content is nearly identical in both acids, with 3.071% in Kuznetsk and 3.079% in Kumuskuduk, indicating similar hydrogen-containing structural groups in both samples. Nitrogen content differs between the two, with 0.93% in Kuznetsk humic acid and 0.63% in Kumuskuduk, potentially reflecting a higher presence of amino groups or proteins in the Kuznetsk sample. The sulfur content in Kuznetsk humic acid (0.391%) is significantly higher than in Kumuskuduk (0.172%), possibly due to a higher concentration of sulfide or organic sulfur compounds. Kumuskuduk humic acid has a higher oxygen content (48.26%) compared to Kuznetsk (45.263%), which may indicate a greater presence of carboxyl groups, enhancing the acidity and reactivity of the substance.

The elemental analysis results suggest that humic acid from the Kuznetsk deposit contains higher levels of carbon, nitrogen, and sulfur, which may indicate a more complex structure and potentially distinct properties compared to humic acid from the Kumuskuduk deposit, characterized by a higher oxygen content. These compositional differences likely stem from variations in the coal formation conditions at these deposits and may influence their respective application areas.

Humic acid from the Kuznetsk deposit is the most suitable for producing organomineral ameliorants. Key reasons include:

– *High carbon content (49.605%):* Carbon forms the organic backbone of humic acids, with a high concentration indicating greater aromaticity and polymerization, enhancing the stability of the organic phase in soil. This structure supports long-term soil improvement and boosts fertility.

– *Elevated nitrogen content (0.93%):* Nitrogen is essential for plant nutrition, and its higher concentration in Kuznetsk humic acids enhances their utility in organomineral fertilizers and ameliorants. This nitrogen content promotes plant growth and optimizes soil agrochemical properties.

– *Sulfur content (0.391%):* Although high sulfur can be unfavorable in some cases, it benefits organomineral ameliorants by supporting amino acid and enzyme synthesis crucial for plants, thus enhancing nutrient availability.

In summary, the balanced composition of Kuznetsk humic acid – with its elevated carbon, nitrogen, and sulfur levels – makes it ideal for organomineral ameliorants, improving soil properties and supplying essential nutrients to plants.

4. Conclusion

The study of lignite from the Kuznetsk and Kumuskuduk deposits yielded valuable insights into their physicochemical characteristics, highlighting their potential for various industrial applications. Key properties, including ash content, moisture, and volatile matter, support the suitability of these coals for use in energy production and industrial processes.

The analysis revealed that lignite from both deposits exhibits low ash content and high volatile matter yield, making it promising for thermal processing techniques such as gasification and pyrolysis. These properties indicate its high potential as a raw material source for the chemical industry, particularly in the production of synthetic gases and liquid hydrocarbons. Elemental analysis, combined with infrared (IR) spectroscopy and thermogravimetric (TG) analysis, provided critical data on the chemical composition and structure of the coals, identifying key functional groups and elemental contents relevant to their industrial potential.

Additionally, humic acids were extracted from coal samples from both deposits using alkaline hydrolysis and further analyzed through elemental analysis, IR spectroscopy, and TG/DSC analysis. The comparative analysis of the physicochemical properties of humic acids from these brown coals revealed substantial differences attributable to the distinct geological formation conditions of the deposits.

Based on the research conducted on humic acids synthesized from brown coals of the Kuznetsk and Kumuskuduk deposits, significant differences in their elemental composition and structural properties were identified. The Kuznetsk-derived humic acid demonstrated higher carbon, nitrogen, and sulfur content, suggesting a more complex molecular structure, with increased aromaticity and polymerization, which are beneficial for soil stability and fertility enhancement. Conversely, humic acid from the Kumuskuduk deposit exhibited higher oxygen content, potentially contributing to greater reactivity in soil applications.

These compositional differences indicate that humic acid from the Kuznetsk deposit is particularly promising for the production of organomineral ameliorants, as its balanced elemental profile enhances its potential as a soil conditioner and nutrient source. The findings of this study highlight the importance of deposit-specific characteristics in determining the suitability of humic acids for various agricultural and environmental applications. Further research could focus on the application-specific performance of these humic acids in soil ecosystems to validate and optimize their use in agronomy.

The findings of this study carry substantial socio-economic implications, particularly within the context of Kazakhstan's growing focus on sustainable development and green technologies. The use of locally available brown coal deposits, such as those from Kuznetsk and Kumuskuduk, as raw materials for the extraction of humic acids presents a cost-effective and scalable alternative to imported organic amendments. This is especially important for Kazakhstan, a country with significant agricultural land and a history of industrial pollution that has impacted soil quality and crop productivity.

By demonstrating the physicochemical suitability of these humic acids – especially the enhanced carbon, nitrogen, and functional group profiles from the Kuznetsk source – this research supports the production of organomineral fertilizers and soil conditioners tailored for Kazakhstan's agro-ecological needs. The potential use of coal combustion ash as a component of such products further increases the economic value chain while promoting waste recycling and pollution reduction.

Table 5 presents how the study relates to and expands upon previous studies. The table highlights the novelty and economic relevance of the findings. In comparison with similar studies – such as Dzheldybaeva et al. (2022) and Kairbekov et al. (2023), who explored humic substances from the

Table 5. Comparative Overview of Humic Acid Research from Kazakh Coal Deposits

№	Study	Coal deposit	Analytical Methods Used	Key Findings	Limitations / Scope	Value Added in Present Study
1	Dzheldybaeva et al. (2022)	Oy-Karagay	Elemental analysis, IR spectroscopy	Confirmed presence of functional groups, antioxidant activity	Limited thermal or morphological analysis	Present study includes TG/DSC for detailed thermal and profiling
2	Kairbekov et al. (2023)	Kiyakty	UV-Vis, IR, elemental analysis	Basic characterization of humic acids and antioxidant potential	No in-depth extraction optimization or application focus	Current research includes extraction efficiency, application potential (e.g., fertilizer use)
3	This Study (2024)	Kuznetsk & Kumuskuduk	IR, elemental analysis, TG/DSC analysis	Comparative evaluation; optimized extraction; functional group quantification; thermal stability	N/A	Introduces dual-site comparison, extraction parameter optimization, socio-economic impact, and direct potential for environmental applications

Oy-Karagay and Kiyakty coal deposits – the present work provides deeper insight into the structural and elemental variations of humic acids, offering a more refined understanding of their functional potential in soil systems. Unlike previous studies that primarily focused on antioxidant activity or basic structural analysis, this study integrates thermal stability, morphological evaluation, and optimized extraction parameters to propose a holistic application framework.

Moreover, the successful implementation of these humic products could reduce dependence on synthetic agrochemicals, decrease the ecological footprint of coal mining, and contribute to rural development through increased soil fertility and crop yields. The government-supported project IRN BR24992961 under which this research was funded illustrates Kazakhstan's strategic commitment to transforming coal waste into high-value agronomic inputs. This aligns with national environmental policy goals and contributes to the broader global objective of advancing circular economy practices in resource-rich developing countries.

Financing

This research was conducted as part of the targeted funding program for the project IRN BR24992961, "Development of new technologies using biological systems for processing coal waste into organo-mineral fertilizer to increase soil fertility and crop productivity".

References (GOST)

[1]. Tyanakh S., Baikenov M.I., Ma Feng Yun, Khamitova T.O., Balpanova N.Zh., Tulebayeva B., Kyzkenova A., Karimova A.B., Rakhimzhanova N.Zh., Kochegina E.V. Kinetic of oil sludge thermolysis process in presence of nickel, cobalt and iron-supported microsilicate // Pol. J. Chem. Technol. – 2023. – Vol. 23, № 3. – P. 101–109.

[2]. Baikenov M.I., Tyanakh S., Ma Feng Yun, Gulmaliev A.M., Makasheva A.M., Khamitova T.O., Malyshev V.P. Viscosity model for the middle fraction of Atasu-Alashankou oil sludge // Mendeleev Commun. – 2024. – Vol. 34, № 3. – P. 446–449.

[3]. Tyanakh S., Baikenov M.I., Gulmaliev A.M., Ma Feng Yun, Musina G., Khamitova T.O., Bolatbay A.N. Kinetics of thermolysis of a low-temperature tar in the presence of a catalyzer agent with deposited metals // Bull. Univ. Karaganda Chem. – 2022. – № 4(108). – P. 89–98.

[4]. Suárez Muñoz M., Melián Rodríguez C., Rudnikas A.G. et al. Physicochemical characterization, elemental speciation and hydrogeochemical modeling of river and peloid sediments used for therapeutic uses // Appl. Clay Sci. – 2015. – Vol. 104. – P. 36–47.

[5]. Chen Y., Banin A., Schnitzer M. Use of the scanning electron microscope for structural studies on soil and soil components // S. E. M. Part 3: Proc. Workshop Techniques for Particulate Matter Studies on SEM. – 1976. – P. 425–432.

[6]. Kairbekov Zh.K. Pererabotka tverdyh gorjuchih iskopaemyh. – Almaty: BTS print, 2014. – 260 s. [in Russian].

[7]. Kairbekov Zh.K., Suimbaeva S.M., Dzheldybaeva I.M., Kairbekov A.Zh., Abil'Mazhinova D.Z. Antioxidant activity and bioavailability of humic substances of low-mineralized sulphide mud // Eng. Sci. – 2023. – № 25. – P. 941–948.

[8]. Dzheldybaeva I.M., Kairbekov Z.K., Maloletnev A.S., Abil'mazhinova D.Z., Suimbaeva S.M. Physicochemical and antioxidant properties of humic substances from coals of the Oy-Karagay and Kiyakty deposits in the Republic of Kazakhstan // Solid Fuel Chem. – 2022. – Vol. 56. – P. 471–477.

[9]. Kairbekov Zh.K., Toktamysov M.T., Zhalgasuly N., Eshova Zh.T. Kompleksnaya pererabotka burykh uglei Tsentral'nogo Kazakhstana (Integrated processing of brown coal from Central Kazakhstan). – Almaty: Izd. KazNU, 2014.

[10]. Arziev Zh.A. Ugli Kyrgyzstana kak osnova dlja poluchenija guminovyh udobreniĭ i stimuljatorov rosta rasteniĭ // Sovrem. probl. nauki i tekhniki: Sb. nauchn. tr. region. nauch.-teoret. konf. – Zhalalabat: Zhalalabatsk. gos. tekhn. in-t, 2002. – № 1. – S. 34–38. [in Russian].

[11]. Feng X., Xiao R., Condé S.M., Dong C., Xun Y., Guo D., Liu H., Liu K., Liang M. Preparation of humic acid from weathered coal by mechanical energy activation and its properties // Minerals. – 2024. – Vol. 14, № 7.

[12]. Ismailov B., Zakirov B., Kadirbayeva A., Koshkarbayeva Sh., Smailov B., Azimov A., Issabayev N. Methods for obtaining phosphorus-containing fertilizers based on industrial waste // Inorganics. – 2023. – Vol. 11, № 6. – P. 1–12.

[13]. Das T., Bora M., Tamuly J., Benoy S.M., Baruah B.P., Saikia P., Saikia B.K. Coal-derived humic acid for application in acid mine drainage (AMD) water treatment and electrochemical devices // Int. J. Coal Sci. Technol. – 2021. – Vol. 8, № 6. – P. 1479–1490.

[14]. Das T., Saikia B.K., Baruah B.P., Das D. Characterizations of humic acid isolated from

coals of two Nagaland coalfields of India in relation to their origin // J. Geol. Soc. India. – 2015. – Vol. 86, № 4. – P. 468–474.

References

[1]. S. Tyanakh, M.I. Baikenov, F.Y. Ma, et al. Kinetic of oil sludge thermolysis process in presence of nickel, cobalt and iron-supported microsilicate. Polish J. Chem. Technol. 23 (3) (2023) 101–109. https://doi.org/10.2478/pjct-2023-0030.

[2]. M.I. Baikenov, S. Tyanakh, F.Y. Ma, et al. Viscosity model for the middle fraction of Atasu-Alashankou oil sludge. Mendeleev Commun. 34 (3) (2024) 446–449. https://doi.org/10.1016/j.mencom.2024.04.043.

[3]. S. Tyanakh, M.I. Baikenov, A.M. Gulmaliev, et al. Kinetics of thermolysis of a low-temperature tar in the presence of a catalyzer agent with deposited metals. Bull. Univ. Karaganda Chem. 4 (108) (2022) 89–98. https://doi.org/10.31489/2022Ch4/4-22-19.

[4]. M.S. Muñoz, C.M. Rodríguez, A.G. Rudnikas, et al. Physicochemical characterization, elemental speciation and hydrogeochemical modeling of river and peloid sediments used for therapeutic uses. Appl. Clay Sci. 104 (2015) 36–47. https://doi.org/10.1016/j.clay.2014.11.029.

[5]. Y. Chen, A. Banin, M. Schnitzer. Use of the scanning electron microscope for structural studies on soil and soil components. In: S. E. M., Part 3: Proceedings of the Workshop on Techniques for Particulate Matter Studies on SEM, 1976, pp. 425–432.

[6]. Zh.K. Kairbekov. Pererabotka tverdyh gorjuchih iskopaemyh. Almaty: BTS Print, 2014, 260 p. (in Russian).

[7]. Zh.K. Kairbekov, S.M. Suimbaeva, I.M. Dzheldybaeva, et al. Antioxidant activity and bioavailability of humic substances of low-mineralized sulphide mud. Eng. Sci. 25 (2023) 941–948. https://doi.org/10.30919/es941.

[8]. I.M. Dzheldybaeva, Z.K. Kairbekov, A.S. Maloletnev, et al. Physicochemical and antioxidant properties of humic substances from coals of the Oy-Karagay and Kiyakty deposits in the Republic of Kazakhstan. Solid Fuel Chem. 56 (2022) 471–477. https://doi.org/10.3103/S0361521921060033.

[9]. Zh.K. Kairbekov, M.T. Toktamysov, N. Zhalgasuly, et al., Kompleksnaya pererabotka burykh uglei Tsentral'nogo Kazakhstana (Integrated processing of brown coal from Central Kazakhstan). Almaty: KazNU, 2014. (in Russian).

[10]. Zh.A. Arziev. Ugli Kyrgyzstana kak osnova dlja poluchenija guminovyh udobreniĭ i stimuljatorov rosta rasteniĭ. In: Sovremennye problemy nauki i tehniki: Sb. nauchn. tr. regional'noĭ nauchn.-teoret. konf., Zhalalabatskiĭ gos. tehn. in-t, Zhalalabat, 2002, 1, pp. 34–38. (in Russian).

[11]. X. Feng, R. Xiao, S.M. Condé, et al., Preparation of humic acid from weathered coal by mechanical energy activation and its properties. Minerals 14 (7) (2024). https://doi.org/10.3390/min14070648.

[12]. B. Ismailov, B. Zakirov, A. Kadirbayeva, et al. Methods for obtaining phosphorus-containing fertilizers based on industrial waste. Inorganics 11 (6) (2023) 1–12. https://doi.org/10.3390/inorganics11060224.

[13]. T. Das, M. Bora, J. Tamuly, et al. Coal-derived humic acid for application in acid mine drainage (AMD) water treatment and electrochemical devices. Int. J. Coal Sci. Technol. 8 (6) (2021) 1479–1490. https://doi.org/10.1007/s40789-021-00441-5.

[14]. T. Das, B.K. Saikia, B.P. Baruah, et al. Characterizations of humic acid isolated from coals of two Nagaland coalfields of India in relation to their origin. J. Geol. Soc. India 86 (4) (2015) 468–474. https://doi.org/10.1007/s12594-015-0334-0.

Сведения об авторах

А.П. Науанова – доктор биологических наук, профессор, Казахский агротехнический исследовательский университет им. Сейфуллина, Астана, Казахстан
E-mail: nauanova@mail.ru
ORCID: 0000-0002-5250-1961

Т.О. Хамитова – PhD, и.о. ассоцированного профессора, Казахский агротехнический исследовательский университет им. Сейфуллина, Астана, Казахстан
E-mail: khamitova.t@inbox.ru
ORCID: 0000-0002-4691-3732

Н. Парманбек – PhD, инженер, Институт ядерной физики, Алматы, Казахстан
E-mail: parmanbek.nursanat@gmail.com
ORCID: 00000-0002-9860-1087

С. Тянах – магистр, докторант, Карагандинский университет им. Е.А. Букетова, Караганда, Казахстан
E-mail: saika_8989@mail.ru
ORCID: 0000-0001-5343-4695

Р.З. Касенов – доцент, Карагандинский университет им. Е.А. Букетова, Караганда, Казахстан
E-mail: r_z_kasenov@mail.ru
ORCID: 0000-0002-9832-5115

С.Ж. Давренбеков – ассоцированный профессор, Карагандинский университет им. Е.А. Букетова, Караганда, Казахстан
E-mail: sdavrenbekov@mail.ru
ORCID: 0000-0002-0218-7062

А.Н. Болатбай – магистр, докторант, Карагандинский университет им. Е.А. Букетова, Караганда, Казахстан
E-mail: abylai_bolatabai@mail.ru
ORCID: 0000-0001-5047-3066

У.Б. Тулеуов – научный сотрудник, НИИ химических проблем, Караганда, Казахстан
E-mail: bekalols1@gmail.com
ORCID: 0000-0002-2664-6884

Синтез и свойства гуминовых кислот, полученных из бурого угля Кузнецкого и Кумускудукского месторождений

А.П. Науанова[1], Т.О. Хамитова[1*], Н. Парманбек[2*], С. Тянах[3*], Р.З. Касенов[3], С.Ж. Давренбеков[3], А.Н. Болатбай[3], У.Б. Толеуов[3]

[1]Казахский агротехнический исследовательский университет им. Сейфуллина, пр. Женис, 62, Астана, Казахстан
[2]Институт ядерной физики, ул. Ибрагимова, 1, Алматы, Казахстан
[3]Карагандинский университет имени Е.А. Букетова, ул. Университетская, 28, Караганда, Казахстан

АННОТАЦИЯ

В данной статье представлены результаты синтеза и сравнительной характеристики гуминовых кислот, выделенных из бурого угля Кузнецкого и Кумускудукского месторождений в Казахстане. Для исследования физико-химических и структурных свойств гуминовых кислот, полученных из этих двух геологических источников, были использованы современные аналитические методы, включая инфракрасную (ИК) спектроскопию, элементный анализ и термогравиметрический/дифференциальный термический анализ (ТГА/ДСК). Результаты показали существенные расхождения в элементном составе, особенно по содержанию углерода, кислорода и водорода, что напрямую связано с геологическими и природными условиями формирования углей. Были выявлены различия в концентрации карбоксильных и гидроксильных функциональных групп, влияющие на сорбционные свойства, кислотность и способность к комплексообразованию гуминовых кислот. Термальный анализ продемонстрировал различную термическую стабильность и характер разложения, отражающие структурную неоднородность образцов. Проведенное исследование подчеркивает важность геологического происхождения при определении функционального потенциала гуминовых веществ и подтверждает возможность их применения в области экологической ремедиации, сельского хозяйства и очистки воды.

Ключевые слова: бурый уголь, гуминовые кислоты, Кумускудукское месторождение, Кузнецкое месторождение, функциональные группы, ИК-спектроскопия, элементный анализ, зольность, реакционная способность.

Кузнецк және құмісқұдық кен орындарының қоңыр көмірінен алынатын гумин қышқылдарының синтезі мен қасиеттері

А.П. Науанова[1], Т.О. Хамитова[1*], Н. Парманбек[2*], С. Тянах[3*], Р.З. Касенов[3], С.Ж. Давренбеков[3], А.Н. Болатбай[3], У.Б.Толеуов[3]

[1]Сейфуллин атындағы Қазақ агротехникалық зерттеу университеті, Жеңіс д., 62, Астана, Қазақстан
[2]Ядролық физика институты, Ибрагимов к., 1, Алматы, Қазақстан
[3]Е.А. Бөкетов атындағы Қарағанды университеті, Университет к., 28, Қарағанды, Қазақстан

АҢДАТПА

Бұл мақалада Қазақстандағы Кузнецк және Күмісқұдык кен орындарынан алынған қоңыр көмірден синтезделген гумин қышқылдарының салыстырмалы сипаттамасы мен талдау нәтижелері ұсынылған. Бұл екі геологиялық көзден алынған гумин қышқылдарының физика-химиялық және құрылымдық қасиеттерін зерттеу үшін инфрақызыл (ИҚ) спектроскопиясы, элементтік талдау және термогравиметриялық/дифференциалдық жылулық талдау (ТГА/ДТА) сияқты заманауи аналитикалық әдістер қолданылды. Зерттеу нәтижелері элементтік құрамда, әсіресе көміртек, оттек және сутек мөлшерінде айтарлықтай айырмашылықтар бар екенін көрсетті, бұл көмірлердің геологиялық және табиғи түзілу жағдайларымен тікелей байланысты. Гумин қышқылдарының сіңіру қабілетіне, қышқылдығына және комплексті түзу мүмкіндігіне әсер ететін карбоксил және гидроксил топтарының концентрациясындағы айырмашылықтар анықталды. Жылулық талдау термиялық тұрақтылық пен ыдырау сипатында айырмашылықтар бар екенін көрсетті, бұл үлгілердің құрылымдық әртүрлілігін көрсетеді. Бұл зерттеу гуминдік заттардың функционалдық әлеуетін анықтауда геологиялық шығу тегінің маңыздылығын айқындап, оларды экологиялық қалпына келтіру, ауыл шаруашылығы және ағын суларды тазарту салаларында қолдану мүмкіндігін растайды.

Түйін сөздер: қоңыр көмір, гумин қышқылдары, Күмісқұдық кен орны, Кузнецк кен орны, функционалдық топтар, инфрақызыл спектроскопия, элементтік талдау, күлділік, реактивтілік.