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Extraction and Characterization of Humic Acid Based on Brown Coal from Kuznetsk Deposit

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Abstract

The scientific novelty of this study lies in a comprehensive analysis of the physical and chemical properties of brown coal of the Kuznetsk deposit using modern research methods. Data on elemental composition, ash content, moisture and volatile matter yield of this coal are systematized and presented. Particular attention was paid to the study of the influence of functional groups on the reactivity of coal, which had not previously been studied in such a detailed form for this deposit. This research uniquely unveils and details the chemical structures of humic acids, offering a more comprehensive understanding of their makeup and functional aspects. The resulting activation energies ranged from 35.65 to 143.9 kJ/mol, with an average of approximately 73.3 kJ/mol, indicating the moderate thermal stability of humic acids derived from the feedstock. Optimal extraction conditions were achieved by treating brown coal from the Kuznetsk deposit with a 4% NaOH solution at 80°C for 2 hours, yielding up to 7% humic acids. Ultrasonic treatment enhanced the physicochemical characteristics of the coal, particularly by increasing the number of oxygen-containing functional groups, as confirmed by IR spectroscopy. The presence of hydroxyl groups was observed in the 3800–3550 cm-1 range, while absorption bands between 1600–1250 cm-1 indicated aromatic structures, suggesting a significant content of stable carbon bonds. The coal exhibited a microporous structure, with pore diameters around 5 nanometers, supporting its high adsorption capacity for gases and liquids. Additionally, nanoparticles approximately 1 nanometer in size were identified, possibly originating from organic matter decomposition or interactions between coal and mineral components, potentially affecting its reactivity. Thus, the research results obtained are a significant contribution to the field of coal chemistry and ecology, and can also serve as the basis for further research and development in the field of the use of humic acids as environmentally friendly additives and sorbents.

Keywords: Brown coal; Humic acids; Kuznetsk deposit; Functional groups; Hydrochloric acid; Infrared spectroscopy; Elemental analysis,; Ash content; Reactivity.
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1. Introduction

Humic acids, as major components of natural humus, participate in various biogeochemical processes. Their different physicochemical characteristics make them a promising resource for applications in agriculture, environmental systems, treatment and industrial processes. Current research on humic acids has been particularly active in recent decades, primarily because of their ability to increase soil fertility, stimulate plant growth, immobilize heavy metals and radioactive isotopes, and exhibit antioxidant and immunostimulatory properties.[1,2]

The classic alkaline extraction scheme (NaOH/KOH) remains a benchmark, but the trend in recent years has been to replace rigid reagents and multi-stage schemes with more stable approaches: deep eutectic solvents (DES/ADES), ionic liquids, ash-gel and hydrothermal routes with ultrasound/microwave intensification. Recent studies show that alkaline DES allow increased yield and adjustment of HA functional composition, and ultrasound activation and statistical design of the experiment give a controlled optimization of process parameters. In parallel, the direction of alternative extractants based on wood ash is developing as an inexpensive and low-toxic "green" extract for the separation of humus substances from peat and lignite.[6,7,8]

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From the point of view of structural analytics, modern protocols recommend combining element analysis (CHNS/O), acid-base titrations, UV-visible spectroscopy (E4/E6, ΔlogK) and molecular weight estimates (GPC), with mandatory verification by vibration and magnetic resonance methods (FTIR, solid and liquid phase ^{13}C-NMR). Recent publications demonstrate the informativity of the ^{13}C-NMR to distinguish the origin of HA and the influence of the extraction method; FTIR remains a working tool for accounting for C= O/C-O/aryl motifs, and thermal analytics (TG/DSC) and conjugated TG-FTIR/DSC give an idea of the thermal stability and decomposition of functional fragments.[9,5,10] Along with the methods of "direct" extraction of HA from brown coals, in recent years, studies of the formation of humus-like substances during hydrothermal conversion of lignocellulose have intensified: it has been shown that the composition of the starting material biopolymers and the process conditions control the formation of HA-like structures. These results are important for comparing natural lignite HA with "engineered" humus materials and for clarifying structure/function markers.[11]

From a practical point of view, studies of the effect of lignite GCs on soil properties, microbiome and crop productivity are relevant: field experiments indicate the possibility of long-term effects during one-time applications, which reinforces the need for standardized quality profiles (acid groups, aromaticity, degree of condensation) for reliable prediction of efficiency.[12]

Thus, the modern agenda in the field of extraction and characterization of humic acids from brown coals includes: the introduction of "green" extractants (DES/ADES, ionic liquids) and energy-efficient intensification (ultrasound, microwaves); statistical optimization of process conditions (multifactor plans, response modeling) to increase the yield and target content of functional groups; multi-method characterization (FTIR, ^{13}C-NMR, TG/DSC, GPC, UV-visible) focusing on structure-property-function linkage; comparison of natural and "engineering" humus materials.[6,5,13,7]

However, to date, the study of the properties of humic acids obtained from brown coal of the Kuznetsk deposit remains an insufficiently studied area. One of the urgent tasks is the development of organomineral fertilizers and ameliorants, including humic substances obtained from brown coal of Kazakhstan, coal ash and effective microorganisms. Kazakhstan has significant reserves of brown coal, which makes it an important source of humic substances that can be used for the production of fertilizers and ameliorants. The use of these natural resources contributes to a rational and environmentally friendly approach to the processing of local natural resources. Utilizing coal ash, a byproduct of the energy sector, in meliorant compositions presents an effective approach to diminish industrial waste volume and mitigate its environmental repercussions. The inclusion of humic substances, coal ash and biological products in fertilizers and ameliorants improves the physicochemical properties of the soil and increases its biological activity, which is especially important for regions with a shortage of organic matter and trace elements. The use of such fertilizers and ameliorants plays a key role in increasing soil fertility, which, in turn, contributes to increased yields and sustainable agricultural development, as well as ensuring food security. In addition, the use of organomineral fertilizers helps to reduce dependence on chemical fertilizers, improving the ecological state and sustainability of agroecosystems.[14-17]

To improve soil health, it is critical to develop reliable and sustainable fertilizers that increase the availability of essential nutrients and humus in the soil. However, often used chelate complexes can accumulate in the soil and leach into water sources, where they increase the mobility of toxic heavy metals and facilitate their absorption by plants. Given the importance of this issue, the researchers aim to create sustainable and effective humic fertilizers that can increase the bioavailability of minerals without posing an environmental threat. This study is aimed at studying the physical and chemical properties of humic acids extracted from brown coal and assessing their practical use.[14,15,16]

This topic is relevant both from the point of view of fundamental science, and from the point of view of practical tasks related to ecology, agriculture and industry. The results of the study can make a significant contribution to the development of methods for processing brown coal and the use of humic substances in various fields. A fundamentally new type of sorbents that can be used to carry out the above processes are humic acids - natural complexing substances. These substances are present in waters, soils, bottom sediments and play an important role in biotransformation processes of organic residues.[17-18] The presence of sufficiently significant reserves of brown coal in Kazakhstan, as a source of humic acids, opens up wide opportunities for the production of humic acids on the territory of the republic and their active use in agriculture and environmental technologies.[17,18]

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The creation of effective organomineral ameliorants based on humic substances and coal ash, which can increase the water-holding capacity of soils and their biological activity, can be a solution to the problem of soil degradation in Kazakhstan[18-20] and other regions similar in climatic conditions, where excessive use of fertilizers, ineffective irrigation and anthropogenic impact are practiced.[21-23]

The resource base of brown coal in Kazakhstan represents a significant potential, which is currently underutilized due to problems with the competitiveness of coal and the environmental consequences of its burning. However, brown coal contains humic acids of interest in agrochemistry and geochemistry. These substances, utilized in organomineral fertilizers, can enhance soil physicochemical properties, and also serve crucial geobiochemical and protective roles vital for biosphere restoration. Using coal ash in meliorants makes the most of secondary resources, sparing waste and lessening its environmental harm.[24-27]

The development and implementation of organo-mineral fertilizers, combining humic substances from brown coal, coal ash and microorganisms, will help improve soil fertility, increase productivity and at the same time reduce dependence on chemical fertilizers. This is especially important for regions with a low content of organic matter and trace elements. This approach allows not only to use existing local natural resources, but also to reduce the volume of industrial waste, directing it to the needs of the agricultural sector.[28-29]

Salinization of soils, especially in the arid regions of Kazakhstan, is another serious problem that requires the search for new solutions. The use of site-specific soil additives based on low-grade coal and bio-solubilizing bacteria improves soil structure and reduces salt levels, which in the long term can restore agricultural productivity and increase agricultural resistance to changing climatic conditions.[30-34]

This paper proposes an ecologically oriented approach to the extraction of humic acids from brown coal of the Kuznetsk deposit using modern experimental planning methods. The properties of the obtained products were compared with the literature data of 2024-2025, which made it possible to identify the features of the functional composition and structural organization. The results obtained contribute to the development of "green" technologies for processing carbon-containing raw materials and can serve as the basis for the development of new areas of use of humic acids in agricultural technologies and environmental engineering.

2. Materials and methods

The object of research in this work is coal mined at the Kuznetsk deposit in the Bukhar-Zhyrau area of the Karaganda region. ‘Razrez Kuznetskiy’ LLP is one of the largest coal mining companies in Kazakhstan and specializes in the extraction of brown coal of the B-3 brand. This coal has specific characteristics, such as low ash content (7.4%), relatively high moisture (9.5%) and a significant yield of volatile matter (47-50%). These parameters make it an important resource for the region's energy and industry.[35,36]

Sample preparation and raw material analysis. At the initial stage of work, samples of brown coal from the Kuznetsk (KUZ) deposits were taken as raw materials for the extraction of humic acids. Each sample was thoroughly crushed on a Vibrator ShchD-6 crusher to 0.5-1 mm to increase the surface area and facilitate extraction (Fig. 1). The carbon samples were then dried in an oven at 80 C for 8 hours to remove moisture

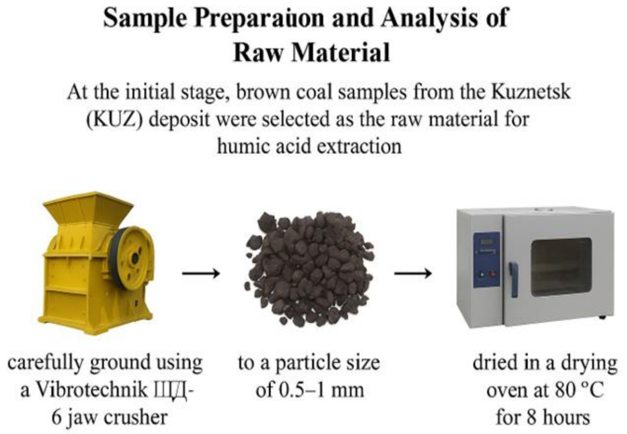


Fig. 1: Crushed and dried samples of coals of Kuznetsk (KUZ) deposit.

Extraction of humic acid from coal by the water-alkaline method. The extraction of humic acids from brown coal utilized a sodium hydroxide-induced aqueous-alkaline process. Upon interaction with sodium hydroxide (NaOH), humic acid compounds undergo chemical transformation, leading to the precipitation of distinct humic acid fractions, as defined by the reaction Eq. (1):

$$\begin{aligned}&\text{Coal} + \text{NaOH}\ \text{HA–COONa} + \text{HMA–COONa} + \text{FA – COONa}\\&2\ \text{HA– COONa} + 2\ \text{HMA – COONa} + 2\text{FA – COONa} + 3\ \text{HCl}\\&2\ \text{HA – COONa} + 2\ \text{HMA– COONa} + 2\ \text{FA – COONa} + 3\ \text{NaCl}\end{aligned} \qquad (1)$$

Humic acids (HA) were extracted by adding NaOH to the carbon samples and then precipitating with an acidic reagent. Extraction of HA was carried out at room temperature (20°C) with aqueous solutions of sodium hydroxides with water during ultrasonic treatment (UST) and settling. The duration of the UST and settling is 5 and 30 minutes, respectively. In the extraction process, 10.0-20.0 g of coal accurately to 0.0001g was placed in a 250 cm^3 flask and 100 cm^3 of 4% sodium hydroxide solution was added. The mixture was heated to 80 °C and stirred on a shaker for 2 hours. The resulting mixture was filtered or centrifuged to separate insoluble coal residues, which were then washed with a small amount of alkaline solution. The remaining coal was dried and weighed for further analysis. The volume of the extracted solution was measured and the content of humic acids in the final product was evaluated (Fig. 2).

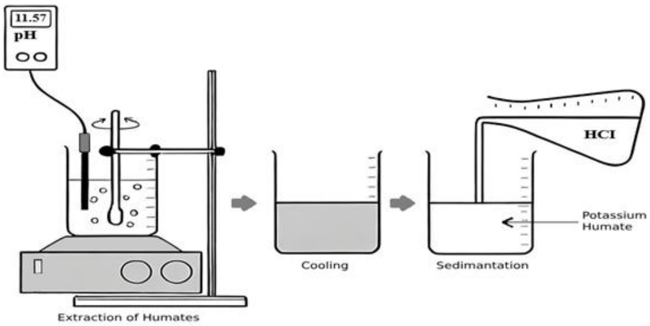


Fig. 2: Process of separation of humic acids from brown coals.

Humic acid was precipitated in a 5% HCl solution, maintaining the pH of the mixture at 2-3. The mixture was allowed to precipitate for 60 minutes, after which the resulting humic acid precipitate was filtered through a pre-weighed filter paper (blue strip). The precipitate was thoroughly washed with distilled water to remove impurities and reagent residues. After completion of filtration, the filter paper with the precipitate was carefully removed from the Buchner funnel, folded into several layers and pre-dried. The filter cake was then placed in a pre-weighed beaker and dried in a drying oven at 80 °C until a constant weight was achieved. This step provided complete removal of moisture from the precipitate and allowed accurate measurement of the mass of humic acid isolated. Ash content of the obtained HA samples was within 8.0-10.0%.

Elemental composition of samples. The elemental composition of the samples was analyzed using a CHNS-O UNICUBE organic elemental analyzer manufactured by Elementar Analysensysteme GmbH (Germany). The principle of operation of the analyzer is based on the classical Dumas-Pregl method, which involves burning samples in the presence of an oxidizing agent in a stream of inert gas. The combustion process was carried out under dynamic conditions involving the supply of a constant flow of oxygen for a given time, resulting in the formation of analytical forms of elements such as carbon dioxide (CO_2), water (H_2O), molecular nitrogen (N_2) and sulfur dioxide (SO_2). Mettler Toledo XPR6U Ultra-Microbalance analytical ultra-microbalances were used to weigh accurate samples. Samples were placed in disposable tin boats less than 0.01 mm thick, which were hermetically sealed with tweezers to prevent sample loss.[37,38] The research work was carried out using the CHNS-O UNICUBE organic element analyzer manufactured by Elementar Analysensysteme GmbH (Germany).

Weighing range: micro (< 1 mg) to macro (about 1 g) application and up to 15 mg of organic substances. Element concentration range:

C: Up to 14 mg absolute or 0-100% (0-50 mg CN *)
H: Up to 2 mg absolute or 0-100%.
N: up to 10 mg absolute or 0-100%.
S: Up to 3 mg absolute or 0-100%.
O *: Up to 6 mg absolute or 0-100%.

Accuracy: < 0.1% absolute (homogeneous), depending on sample type, assay mode and configuration. The samples were burned in a quartz reactor used in a Unicube analyzer (ELEMENTAR) with a ceramic coating resistant to high temperatures. This allowed combustion at temperatures up to 1150 °C without the use of catalysts.

The temperature of the oxidation column was 1150°C and that of the reduction column was 850°C. Each sample was analyzed three times, after which the results were averaged. The sulfonamide standard (Elementar Analysensysteme GmbH) was used to calibrate and verify the accuracy of the equipment. During the measurements, tin boats of 4 × 4 × 11 mm in size and high purity gases were used: helium (99.9999%) and oxygen (99.999%). The main standard is ASTM D5373, which regulates methods for determining the content of carbon, hydrogen and nitrogen in coal and coke.[39,40]

Thermal decomposition of the mixture was carried out using a LabsysEvoTG-DTA/DSC derivatograph in corrundle crucibles in the temperature range from 30 to 600 °C in an argon stream (the flow rate of the protective and purge gas was 20 and 50 ml per minute, respectively). The measurement results were processed using the "OriginLab" software package and the "PythonAnaconda3" distribution.

In differential scanning calorimetry, thermal differences between a sample and a reference are detected by quantifying the differential heat flux as a function of temperature. Both sample and reference are thermally equilibrated at identical temperatures throughout the experimental process.

Characteristically, the temperature protocol for differential scanning calorimetric analysis is characterized by a linear temperature rise as a function of time for the sample container. The reference sample must have a well-defined heat capacity within the thermal scanning mode.[41,42]

Samples of coals and humic acids weighing 10 mg were placed in aluminum oxide crucibles and heated at a constant rate of 10 °C/min in an air atmosphere to a temperature of

800°C. In the process, changes in the mass of the sample were measured, which made it possible to determine the temperatures at which the main stages of decomposition of organic matter occur, as well as the content of moisture, volatile substances, fixed carbon and ash. TGA also made it possible to evaluate the stability of the organic components of coal and its possible reactivity. Mass calibration was performed using calcium carbonate standard ($CaCO_3$), heat calibration using indium (In).

Determination of the composition of humic acids using the proton nuclear magnetic resonance (^{1}H NMR) method provides an opportunity to study in detail the structure of humic acids, their functional groups and the distribution of various types of hydrogen atoms (protons) in the molecule. This method reveals information about the chemical environment in which protons are located, as well as their interactions with neighboring atoms in the structure of the molecule.[38]

To analyze the structure of humic acid samples, NMR spectroscopy was performed using a JNM-ECA 500 NMR spectrometer from JEOL (Japan). The proton nuclear magnetic resonance (^{1}H NMR) analysis process involves several key steps. At the first stage, the samples are prepared for analysis, then they are exposed to a strong magnetic field. As a result of the interaction of hydrogen nuclei with the magnetic field, resonant absorption of radio frequency radiation occurs, which is recorded by a spectrometer. The obtained data make it possible to interpret the spectra, which gives in-depth information about the structure of humic acid molecules, their functional groups and the spatial arrangement of hydrogen atoms.

A scanning electron microscope MIRA3 (TESCAN, Czech Republic) was used to study the surface morphology of coal and humic acids. This microscope has a high resolution, which allows a detailed analysis of the microstructure of samples at the micron and submicron levels. Analysis of the particle size and morphology of coals and humic acids was carried out with an increase × 6920 and × 17300.

Antioxidant activity of coals and HA was determined by cathodic voltammetry. The basis of this method is the process of electroreduction of oxygen, which proceeds on the electrode by a mechanism similar to the restoration of oxygen in tissues and cells of the body.

The methodology for determining the activity of the investigated substances in relation to the electroreduction (ER) of O_2 is as follows. First, voltammetry current voltammetry of O_2 ER in the absence of the test substance is recorded. Then the investigated substance is added to the cell in the volume of 0.5 ml aliquot, after which cathodic voltammetry of O_2 ER is taken under the same conditions. Measurements were repeated at least 3 times after a certain time interval, and each time the value of the limiting current of O_2 ER was estimated. The studies were conducted on a voltammetric STA-2 antioxidant activity analyzer (Polyant NPP, Tomsk, Russia) connected to a personal computer. The work used a continuous current mode of cathode voltammetry, a potential sweep rate W = 30 mV/s, an operating potential range from 0.0 to -0.8 V, a solution mixing time of 20 seconds, and a soothing time of 10 seconds. The electrochemical cell was a glass cup with a background electrolyte solution and electrodes immersed in it. For measurements, an indicator mercury-film electrode was used, chloride-silver electrodes were used as a reference electrode and an auxiliary electrode. A 0.1 M alcoholic solution of sodium perchlorate was used as the background solution. Ethanol was selected for the preparation of standard solutions of coals and humic acids. Use of said solvent enables to obtain aqueous-organic mixtures with considerable content of humic substances without separation. The basic standard solution was prepared by dissolving a 0.02 g sample of the substance in 10 mL ethanol.[39,40]

The coal was sonicated using a MOD MEF-91 ultrasonic disperser using 20 amps at 40 kHz and 120 watts at 50°C. 20% aqueous carbon slurry diluted at the 1:5 solid to liquid ratio was sonicated for 20-60 minutes. Ultrasound promotes mass transfer, accelerates chemical reactions of coal and causes intense bubble vibrations, promoting the formation and propagation of cracks. This leads to an increase in the permeability of coal, since sharp edges and corners are divided into rounded particles with smooth surfaces, which is facilitated by the dispersion of fragments of low hardness coal.[43]

Antioxidant activity of coals and HA was determined by cathodic voltammetry. The basis of this method is the process of electroreduction of oxygen, which proceeds on the electrode by a mechanism similar to the restoration of oxygen in tissues and cells of the Eq. (2):

$$\begin{aligned} &O_2 + e \Leftrightarrow O_2^{\cdot -} \\ &O_2^{\cdot -} + H^+ \Leftrightarrow HO_2^{\cdot} \\ &HO_2^{\cdot} + H^+ + e \Leftrightarrow H_2O_2 \\ &HO_2^{\cdot} + H^+ + e \Leftrightarrow H_2O_2 \end{aligned} \tag{2}$$

The methodology for determining the activity of the test substances relative to O_2 ER is detailed below. Initially, current voltammograms of O_2 ER are obtained without the test substance. Subsequently, a 0.5 mL aliquot of the test substance is introduced, followed by capturing cathode voltammograms of O_2 ER under identical conditions. These measurements are repeated a minimum of three times at set intervals, and the O_2

Table 1: Average values of oxygen (O), carbon (C), hydrogen (H), nitrogen (N) and sulfur (S) content in brown coal of the Kuznetsk deposit and ash obtained during its combustion.

NO.	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

ER limiting current value is calculated for each instance.

An indicator that the test samples exhibit antioxidant activity is a decrease in O_2 ER current in its absolute value.

Antioxidants of reducing nature are expected to react with oxygen and its active radicals on the surface of the indicator electrode. The degree of decrease in O_2 EV current was an indicator of the antioxidant activity of the test sample. The antioxidant activity coefficient of the samples, K, μmol/(L ≤ min), was calculated using the Eq. (3):

$$K=\frac{C_{O_2}}{t}\left(1-\frac{I_i}{I_o}\right) \tag{3}$$

Where Co_2 – concentration of oxygen in the initial solution without substance, μmol/L;
Ii – current value of limit current of O_2 ER, μA;
Io - value of limit current of O_2 ER in the absence of substance in solution, μA;
t - process time, min.

The results obtained were subjected to statistical processing. The results were processed according to known equations as follows:

$$K_{cp} \text{ – mean value, calculate: } \overline{X}=\frac{\sum_{i=1}^{n} X_i}{n} \tag{4}$$

S – standard deviation, calculated from the Eq. (5):

$$S_i=\sqrt{S_i^{2}}=\sqrt{\frac{1}{n-1}\sum_{j=1}^{n}(Y_{ij}-\overline{Y}_i)^2} \tag{5}$$

Sr – relative standard deviation, calculated: $S_r=\frac{S}{\overline{X}}$

Analysis of data was performed using analysis of variance, correlation and regression analysis, and other statistical methods that ensure the reliability and accuracy of the results.[44-49]

3. Results and discussion

The Kuznetsk coal sample has specific properties, including low ash content (7.4%), relatively high moisture content (9.5%), and significant volatile matter yield (47-50%). These indicators determine its importance as a valuable energy resource with high combustion efficiency, which determines its demand in the energy sector and industry of the region.

Elemental analysis to determine the content of carbon, hydrogen, nitrogen and other elements. Using the element analyzer CHNS-O UNICUBE (Elementar Analysensysteme GmbH), the contents of carbon (C), hydrogen (H), nitrogen (N), sulfur (S) and oxygen (O) in various samples were determined. Based on the analysis, the average values of oxygen (O), carbon (C), hydrogen (H), nitrogen (N) and sulfur (S) in the brown coal of the Kuznetsk deposit (sample Kuz-2024) and in ash formed after its combustion (sample Zola Kuz-2024) were obtained. The data obtained are presented in Table 1.

The brown coal of the Kuznetsk deposit is characterized by a high carbon content (56.02%), which confirms its high calorific value and makes it suitable for use as a fuel. A high content of oxygen (25.07%) and hydrogen (5.085%) indicates the presence of a large amount of volatile substances and a high reactivity during combustion, which increases its efficiency during the combustion process. The absence of nitrogen in the sample indicates a low risk of formation of nitrogenous compounds, such as nitrogen oxides (NO_x), which has a positive effect on the environmental safety of its use. A low sulfur content (0.155%) indicates a low probability of sulfur dioxide (SO_2) emissions, although control of SO_2 emissions during combustion still remains important to prevent air pollution.

In the ash sample, there is a significant decrease in the content of oxygen (up to 11.56%), carbon (up to 12.33%) and hydrogen (up to 0.16%) compared to the original coal. This indicates that most of the oxygen and hydrogen has been released as combustion gases such as carbon dioxide (CO_2) and steam (H_2O). The carbon content of the ash at 12.33% indicates the presence of residual organic matter that may be useful for the use of ash as a component of organ mineral fertilizers. The nitrogen content in the ash (0.43%) is due to the possible formation of nitrogenous compounds (NO_x) when burning coal in air.

The decrease in oxygen and carbon content after combustion is due to the fact that most of these elements passed into combustion gases. The carbon content in the ash remains at the level of 12.33%, which indicates its incomplete oxidation, which may be useful for the further use of ash. Hydrogen, the content of which in coal was 5.085%, almost completely disappears (0.16%) in the ash, which is associated with the evaporation of hydrogen in the form of water vapor. The sulfur content, fixed at 0.155% in coal, is completely absent in the ash, which indicates its evaporation during combustion in the form of gaseous compounds such as SO_2.

Ash formed after burning lignite has the potential to be used as a component of organomineral ameliorants. The residual content of carbon and nitrogen can help increase the fertility of the soil, improving its structure. The absence of sulfur in ash is a positive factor from an environmental point of view, since a high sulfur content could lead to soil acidification. The low content of hydrogen and oxygen in the ash indicates its mineral nature, which can also have a positive effect on the physicochemical characteristics of the soil.

Thus, the ash of brown coal of the Kuznetsk deposit can be used to improve soils, however, for the final assessment of its suitability, additional studies are needed for the presence of heavy metals and toxic elements.

Identification of functional groups. An FSM 1202 IR spectrometer was used to identify the functional groups present in the samples. For this, the carbon samples were ground and mixed with KBr (potassium bromide) to form tablets. The spectra were taken in the range of 4000-400 cm $^{-1}$ with a resolution of 4 cm $^{-1}$. The focus was on the absorption bands characteristic of various functional groups such as carboxyl groups (-COOH), hydroxyl groups (-OH), aromatic bonds (C = C) and aliphatic hydrocarbon chains (C-H). The data obtained are presented in Fig. 4.

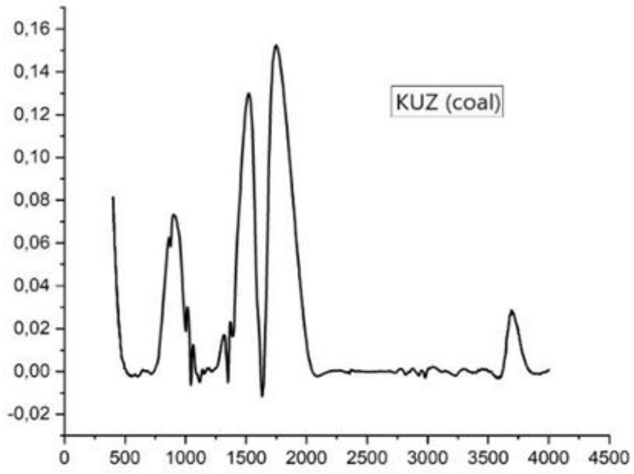
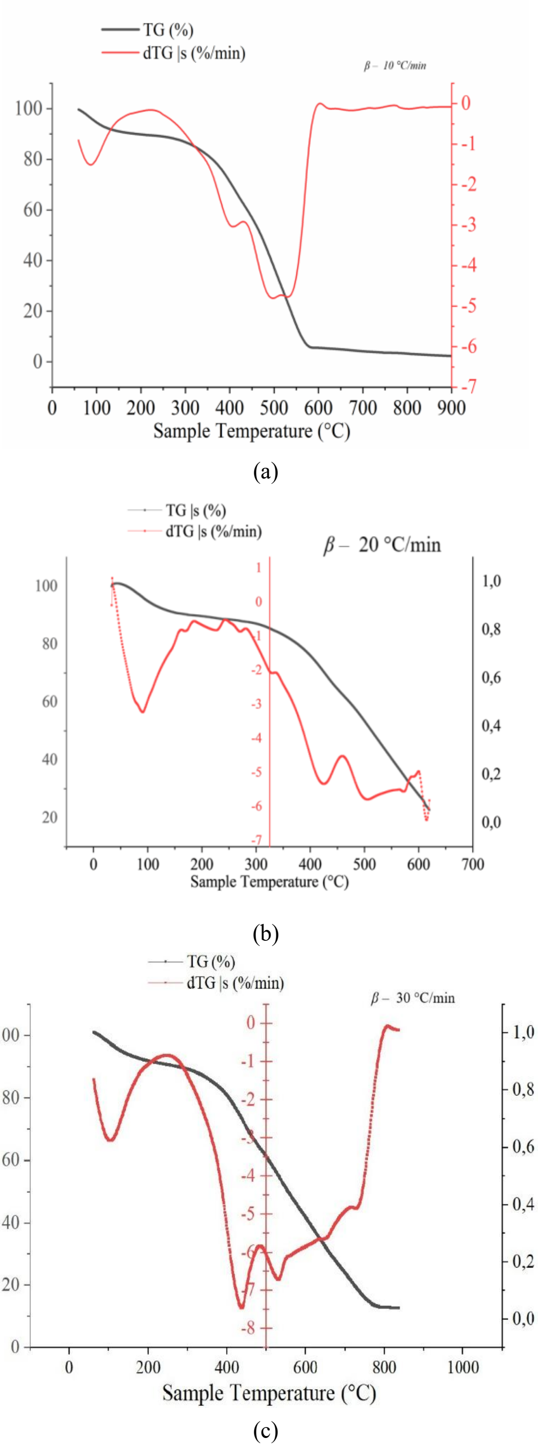


Fig. 3: Infrared spectra of coal samples.

As can be seen from Fig. 3, the band in the region of 3800-3600 cm^{-1} indicates water bound to the surface of the coal or hydroxyl groups formed during chemical reactions. In the range 2000-1600 cm^{-1}, absorbances associated with fluctuations in C = O bonds are observed. These may be carbonyl compounds such as ketones, aldehydes or carboxyl groups. In coals, such bands can arise due to the presence of oxygen-containing functional groups that participate in oxidation processes. The band in the region of 1600-1300 cm $^{-1}$ is responsible for the deformation vibrations of C-H and C = C bonds in aromatic rings. Coals contain a large number of aromatic structures, and this range may indicate the degree of aromaticity of the carbon skeleton of the coal. The more intense the bands in this range, the higher the aromatic carbon content. A range of 1000-750 cm^{-1} may indicate the presence of substituted benzene rings (aromatic hydrocarbons) and C-H fluctuations in the plane of the ring. Also, there may be fluctuations in carbon-oxygen bonds in structures such as ethers or alcohols, if present in coal.



(a)

(b)

(c)

Fig.4: TG/DSC curves of Kuznetsk coal at different heating rates: (a) 10 °C/min, (b) 20 °C/min, and (c) 30 °C/min.

Differential scanning calorimetry (TGA)/DSC analysis. The curves of sample weight loss versus temperature are shown in Fig. 5 at a heating rate of β - 10 °C/min, β - 20°C/min, β - 30 °C/min at a range from 140 to 480°C using the Ozawa-Flynn-Wall method (OFW). The reactivity of a substance can

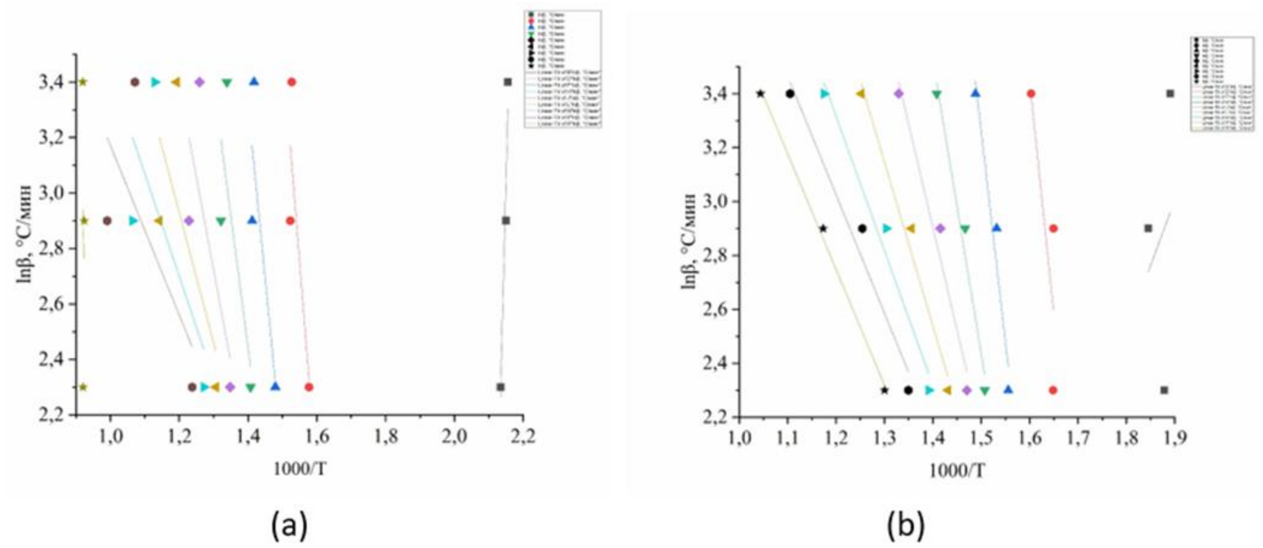


Fig. 5: Dependence of the logarithm of the heating rate on the return temperature.

be characterized by the value of the activation energy.

The determination of the activation energy was based on the generalized Eq. (6) of the solid phase reaction rate under non-isothermal conditions:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} e^{\left(\frac{-E_a}{RT}\right)} f(\alpha), \tag{6}$$

Where α – degree of conversion of raw materials; β – linear rate of heating of samples, °C/мин; A – pre-exponential factor, s^{-1}; T – absolute temperature, K; E – activation energy, kJ/mol; R – universal gas constant, J/mol K, $f(\alpha)$ – mathematical model of a dimensionless kinetic function, depending on the type and mechanism of the reaction. The α value in Eq. (6) is the relative degree of conversion of starting material (coal and humic acid) defined as $\alpha = \frac{m_s - m}{m_s - m_f}$, where m_s and m_f are the initial and final mass of the substance, m is the mass of the substance at the point of measurement.[18]

Ozawa-Flynn-Wall method. According to the Ozawa-Flynn-Wall method of non-isothermal kinetics, when integrating and then logarithm Eq. (6), we obtain Eq. (7):

$$\ln G(\alpha) = \ln\left(\frac{AE}{R}\right) - \ln\beta + \ln p(z), \tag{7}$$

$G(\alpha)$ for the first-order reaction is Eq. (8):

$$\int_0^a \frac{d\alpha}{f\alpha} = \int_0^a \frac{da}{1-a} = -\ln(1-a); \qquad p(z) = \frac{e^{-z}}{z} - \int_{-\infty}^{z} \frac{e^{-z}}{z} dz; z = \frac{E}{RT}. \tag{8}$$

Using the Doyle approximation,[24] we obtain Eq. (9) to substitute into the Eq. (7):

$$\ln p(z) = -5.3305 - 1.052z. \tag{9}$$

The OFW method is based on the assumption that the reaction rate at a constant α value depends only on temperature. The following equation is used in the analysis of non-isothermal kinetics:

$$\ln \beta_i = \ln\left[\frac{A_\alpha E_a}{Rg(\alpha)}\right] - 5.331 - 1.052 \frac{E_a}{RT_{\alpha,i}}. \tag{10}$$

substitution Eq. (7) and (9) gives the OFW Eq. (4) for calculating the dependence of the thermal destruction rate from the brown coal of the Kuznetsk deposit and humic acid from the brown coal of the Kuznetsk deposit on the return temperature, the activation energy was calculated.[50]

During thermal analysis of humic acids isolated from brown coal of the Kuznetsk deposit, thermograms TG and DSC were obtained at different heating rates: 10, 20 and 30°C/min. Based on the thermograms, the maximum decomposition temperatures at each heating rate were calculated and used to determine the activation energy by the Ozawa-Flynn-Wall (OFW) method.[51]

TG/DSC analysis was performed on a LABSYS^{TM}EvoTG-DTA/DSC instrument (SETARAM, France) to evaluate the thermal stability of the test samples and study their decomposition under heat. The coal samples were placed in alumina crucibles and heated at a constant rate of β – 10°C/min, 20°C/min, 30 °C/min in an air atmosphere to a temperature of 800°C. In the process, changes in the mass of the sample were measured, which made it possible to determine the temperatures at which the main stages of decomposition of organic matter occur, as well as the content of moisture, volatile substances, fixed carbon and ash. TGA also made it possible to evaluate the stability of the organic components of coal and its possible reactivity. The data obtained are presented in Fig. 4.

From Fig. 4, it can be seen that the first stage of weight loss was observed at a temperature of 100-150°C, which corresponds to moisture evaporation. The second stage at a temperature of 200-400 °C corresponds to the release of volatile substances, such as low molecular weight hydrocarbons and other organic compounds. The third stage, at a temperature of 400-600°C, is associated with the decomposition of the main organic matrix of coal, including the decomposition of complex macromolecules of humic substances and hydrocarbons. The remaining weight of 600-800°C corresponds to the mineral content (ash), which was also confirmed by the ash residue after TGA analysis.

TG/DSC analysis of Kuznetsk coal at different heating rates (β = 10 °C/min, 20 °C/min, and 30°C/min) (Figure 4). The thermogravimetric (TG) and differential scanning calorimetry (DSC) curves of Kuznetsk coal were recorded at three different heating rates: 10 °C/min, 20 °C/min, and 30 °C/min. The TG curves show a consistent pattern of mass loss corresponding to moisture release, volatile matter decomposition, and fixed carbon combustion. As the heating rate increases, the decomposition temperatures shift slightly to higher values due to thermal lag. The DSC curves display exothermic peaks associated with the combustion of volatiles and fixed carbon. At higher heating rates, these peaks become more intense and occur at higher temperatures, indicating a kinetic effect on thermal behavior. Thermogravimetric (TG) and differential scanning calorimetric (DSC) analyses of Kuznetsk coal were conducted at three heating rates: 10, 20 and 30°C/min. The obtained thermograms demonstrate a characteristic dependence of thermal behavior on the heating rate. At a rate of 10 °C/min, the main mass loss is observed in the temperature range of 300-500 °C, which is associated with the removal of volatiles and the thermal decomposition of organic components. The exothermic peak on the DSC curve is fixed in the region of 400-500 °C, corresponding to the oxidation reaction. An increase in the heating rate to 20 °C/min leads to a shift of both TG and DSC curves to the region of higher temperatures: decomposition begins at 350 °C, and exothermic effects appear in the range of 450-550 °C, becoming more intense. At a rate of 30 °C/min, decomposition processes occur most sharply - the main degradation of the mass is observed in the range of 400-600 °C, and the DSC curve shows pronounced exothermic peaks in the range of 500-600 °C. Thus, an increase in the heating rate contributes to the intensification of thermal processes, but causes a shift in reaction temperature intervals and a decrease in the uniformity of decomposition of coal. Figures present the thermogravimetric (TG) and differential scanning calorimetry (DSC) curves of Kuznetsk coal obtained at different heating rates: 10, 20, and 30 °C/min. The analysis reveals that increasing the heating rate significantly affects both the temperature range and the intensity of thermal processes. At 10 °C/min, the main weight loss occurs between 300–500 °C, while exothermic effects are observed within 400–500 °C, corresponding to the release of volatile matter and oxidation of organic components. When the heating rate is increased to 20 °C/min, thermal decomposition begins at around 350 °C, and more intense exothermic peaks appear between 450–550 °C. At the highest rate of 30 °C/min, decomposition occurs most rapidly: major mass loss is observed between 400–600 °C, with sharp exothermic effects recorded in the 500–600 °C range. Thus, increasing the heating rate intensifies thermochemical reactions, though it also shifts the process to higher temperatures, indicating potential limitations in internal heat transfer within the sample. The thermogravimetric (TG) and differential scanning calorimetry (DSC) curves of Kuznetsk coal at different heating rates—10, 20, and 30 °C/min—are shown in the figures. The results indicate that increasing the heating rate significantly affects the thermal decomposition behavior and intensity of the exothermic reactions. At a heating rate of 10 °C/min, the primary weight loss occurs between 300–500 °C, and exothermic effects are observed within 400–500 °C, corresponding to the release of volatiles and initial oxidation of the organic matter. When the rate is increased to 20 °C/min, thermal decomposition begins around 350 °C, and more intense exothermic peaks are observed in the 450–550 °C range. At 30 °C/min, decomposition proceeds rapidly with major weight loss between 400–600 °C, accompanied by strong exothermic reactions around 500–600 °C. These shifts indicate an acceleration of thermochemical processes at higher heating rates, along with possible limitations in internal heat transfer within the sample.

Table 2: Summary of TG/DSC analysis parameters of Kuznetsk coal at different heating rates.

Heating rate (°C/min)	TG weight loss range (°C)	DSC exothermic peak (°C)	Process characteristics
10	300–500	400–500	Volatile release, mild oxidation
20	350–550	450–550	More intense decomposition and oxidation
30	400–600	500–600	Rapid decomposition, limited heat transfer

Increasing the heating rate shifts the decomposition temperature range and enhances exothermic reactions.

Corresponding graphs were plotted for each α conversion level. Fig. 5 (a, b) shows a series of lines characteristic of different degrees of α transformation. The slope angles of the lines allow you to calculate the activation energy. The calculation results are shown in Table 3-4.

As a result of thermal analysis of humic acids isolated from brown coal of the Kuznetsk deposit, thermograms TG and DSC were obtained at various heating rates: 10, 20 and 30 °C/min. Based on these thermograms, the maximum decomposition temperatures were determined, which were used to calculate the activation energy by the Ozawa-Flynn-Wall (OFW) method (Figure 6a). Calculations have shown that activation energy values vary in a wide range - from 24.7 to 361.8 kJ/mol, depending on temperature. At the initial stage (T = 350°C), a high value of activation energy (249.8 kJ/mol) is observed, which indicates thermally stable components, probably including strongly crosslinked or aromatic structures. As the temperature increases (up to 700 °C), a consistent decrease in activation energy is observed to a minimum value of ~ 24.7 kJ/mol, which corresponds to the destruction of less stable functional groups and aliphatic chains.

Table 3: Activation energy from brown coal of Kuznetsk deposit by the Ozawa-Flynn-Wall method.

Tmax (°C)	Tmax (K)	Slope	Ea (kJ/mol)
350	623.15	48.25982	-249.78
400	673.15	-15.46337	86.44
450	723.15	-12.62925	75.23
500	773.15	-9.52277	59.92
550	823.15	-6.66630	45.56
600	873.15	-4.70264	34.15
650	923.15	-3.68857	28.32
700	973.15	-3.05622	24.70
750	1023.15	-42.48909	361.84

Table 4: Ozawa-Flynn-Wall humic acid activation energy.

α	Slope of line	E (kJ/mol)	R^2
0.1	- 17.30	151.4	0.695
0.2	- 15.64	136.7	0.953
0.3	- 10.91	95.5	0.975
0.4	-7.64	66.8	0.968
0.5	- 6.08	53.2	0.980
0.6	- 4.99	43.7	0.974
0.7	- 4.40	38.6	0.968
0.8	- 4.29	37.7	0.997

However, with a further increase in temperature to 750 °C, a sharp increase in activation energy to 361.8 kJ/mol is observed. This may indicate the presence of residual high molecular weight structures resistant to thermal decomposition, or the beginning of the processes of aromatization or graphitization of humus residues. The results obtained indicate a complex multi-stage nature of the thermal decomposition of humic acids due to their heterogeneous structure and a variety of functional groups. The Ozawa-Flynn-Wall method has demonstrated its effectiveness for estimating the kinetic parameters of the thermal destruction of humic substances without the need to specify the reaction mechanism.

The obtained activation energy values indicate the multi-stage nature of the thermal decomposition of humic acids. In the initial stages (α = 0.1-0.2), the activation energy reaches values above 130 kJ/mol, which may be associated with the breaking of the strongest bonds. Subsequently, a decrease in activation energy is observed, indicating easier processes of degradation and destruction of side chains. Analysis of DSC curves showed the presence of one main endothermic effect in the region of 220-270 °C, which corresponds to the main phase of humic acid decomposition. Additional mild effects may be due to the removal of moisture and volatile components in the early stages of heating. The obtained activation energy values ranged from 35.65 to 143.9 kJ/mol, with an average value of about 73.3 kJ/mol, which indicates moderate thermal stability of humic acids from this raw material (Fig. 5 b).

Thus, the results of thermal analysis confirmed the complex structure of humic acids and their multi-stage degradation upon heating. The activation energy was calculated using the Ozawa-Flynn-Wahls method. The average activation energy was 73.3 kJ/mol, which indicates moderate thermal stability of humic acids from this raw material. The OFW method demonstrated a high degree of consistency in calculating the activation energy, as evidenced by the high values of the coefficient of determination (R^2).

Calculation of the quantitative yield of humic substances from coal waste. As a result of the experiments, humic acids were extracted from coal samples from the Kuznetsk deposits by alkaline hydrolysis. 0.7 g of humic acids were obtained from the coals of the Kuznetsk deposit weighing 10 g (yield 7%) (Fig. 6).

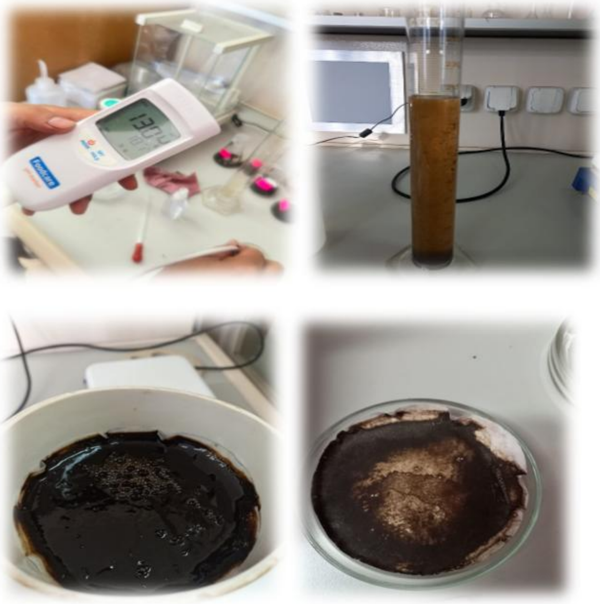


Fig. 6: Acidification and precipitation of humic acids.

In order to find the most optimal conditions for the humic acid extraction technology, various parameters of the main components of the process were studied. Thus, during the extraction of humic acid, an alkali solution with a concentration of 1% to 4% was used. The process was carried out in the temperature range from 20 to 80 °C. The reaction time was 30-120 minutes.

Studies have shown that using a high concentration of alkali leads to a more complete reduction of humic acids. However, when the treatment temperature exceeds 80 °C, the yield of sodium humates significantly decreases from 4% to 2%. At the same time, due to hydrolysis and leaching of carboxyl and polysaccharide fragments (which leads to an increase in the relative content of aromatic structures to 44-45%), the composition of the products changes significantly. An increase in time over 2 hours did not significantly affect the result.

Thus, it has been found that the most effective conditions for complete separation of sodium humate are an alkaline concentration of 4%, a temperature of 80°C and a reaction time of 120 minutes.

Spectroscopic evaluation of humic substances and structural characterization study. As a result of the experiments, humic acids were extracted from coal samples from the Kuznetsk deposits by alkaline hydrolysis. The obtained humic acid samples were analyzed by IR and TG/DSC analysis (Fig. 7, 8).

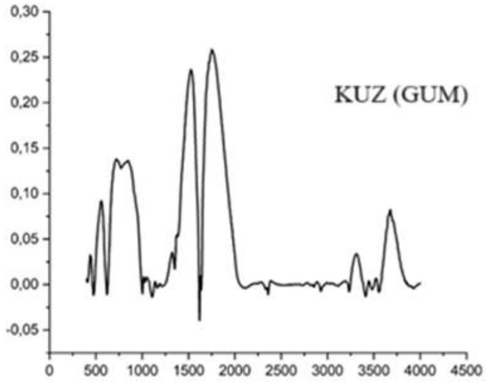


Fig. 7: IR spectra of the obtained humic acids.

Fig. 7 shows that in the range of 3800-3550 cm^{-1} there is an absorption band associated with fluctuations in O-H groups. These bands are characteristic of hydroxyl groups (both in free water and in hydrogen bonds), which are present in the structure of humic acids. At 2100-1600 cm^{-1}, absorption bands belonging to carboxylic acids, aldehydes, ketones and esters are observed. The range of 1600-1250 cm^{-1} is responsible for the fluctuations of aromatic C = C bonds, which is characteristic of humic acids, which have aromatic rings in their structure. Also, deformation fluctuations of C-O bonds in carboxyl and phenolic groups can be manifested here, which indicates the presence of complex oxygen-containing functional groups in humic acids. At 1000-600 cm^{-1}, absorption bands associated with C-H deformation oscillations in aromatic rings can be observed, as well as oscillations of C-O-C bonds in esters and ester groups. The low frequency range of 600-500 cm^{-1} is associated with vibrations outside the C-H plane in aromatic systems, as well as vibrations associated with deformations of C-C bonds in carbon chains. Thermogravimetric analysis of humic acids was carried out in an inert medium to a temperature of 1000 °C.

Determination of the functional groups of coal is important for understanding its reactivity, sorption, combustion, coking and other technological processes. The study of the composition of the functional groups of coal at the Kuznetsk deposit allows us to assess its potential as a fuel and raw material for the chemical industry, as well as choose the best methods for its processing

The methods described above provide a comprehensive approach to the study of coal and help to better understand its chemical nature and potential for use in various industries. The data obtained are presented in Fig. 8.

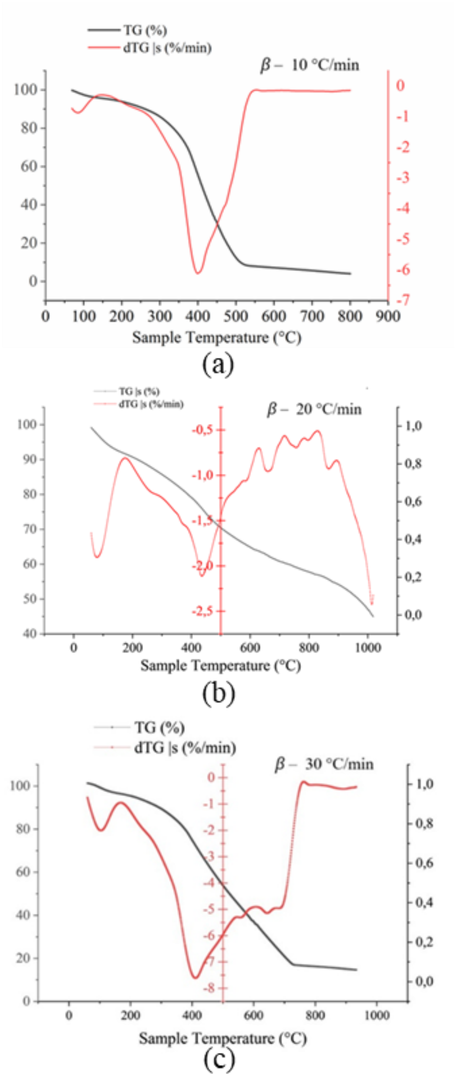


Fig. 8: TG/DSC results for humic acid samples (KUZ) at the rate β – 10 °C/min, 20 °C/min, 30 °C/min.

As can be seen from the curves of thermogravimetric analysis of humic acids in the range of 30 ~ 175°C, a slight

Table 5: Comparative table and schematic summary for TG/DSC data of humic acid from Kuznetsk coal at three heating rates.

Parameter	10 °C/min	20 °C/min	30 °C/min
Start of moisture removal (TG)	~100–120 °C	~120–130 °C	~130–150 °C
Main start of decomposition (TG)	~200 °C	~250 °C	~280 °C
Completion of main decomposition	~500–550 °C	~550–600 °C	~600–650 °C
Exothermic DSC peak maximum temperature	~330–350 °C	~360–380 °C	~390–410 °C
Residual weight after 700-800 ° C	~45–50 %	~45–50 %	~45–50 %
Features	Less displacement, more blurred peaks	Pronounced, shifted peaks	Sharper and higher temperature peaks

change in mass is probably associated with water residues. Further, the decomposition of the sample takes place in two stages. The first step at 200 ~ 500°C is followed by the decomposition of highly volatile substances and functional groups such as carboxyl, phenol and methoxy groups. Also, small organic molecules associated with aromatic structures are destroyed, which leads to significant mass loss. This stage is characterized by the release of water, carbon dioxide and other low molecular weight gases. Further, at temperatures of 550 ~ 1000 °C, more stable aromatic structures and condensed polycyclic systems are destroyed. This results in further weight loss and carbon residue formation. Major processes include carbonization (conversion of organic matter to carbon) and the formation of a stable residue resembling coke. These steps reflect the sequential thermal degradation of humic acids, ranging from light functional groups to stable carbon structures.At a heating rate of β = 10 ° C/min (a): the TG curve (thermogravimetric analysis) shows a smooth decrease in sample weight in several steps. The first stage - mass loss up to ~ 150 ° C - is probably due to the removal of moisture and volatile components. The main decrease in mass occurs in the range of 200-500 °C, which is associated with the thermal decomposition of organic substances of humic acid (destruction of functional groups, destruction of the structure). After 600°C, the rate of mass decline decreases, indicating the formation of more stable carbonaceous residues. The DSC curve (differential scanning calorimetry) shows an endothermic peak at a ~ of 100-120°C (water evaporation) and exothermic processes in the range of 300-500°C (decomposition of organic components). At a heating rate of β = 20 ° C/min (b): With an increase in the heating rate, the onset of mass loss and thermal effects shifts towards higher temperatures. Dehydration (loss of water) occurs at a slightly higher temperature (~ 130 °C). The main thermal decomposition starts later (from about 250 °C) and ends at temperatures above 550 °C. Exothermic peaks on the DSC become more pronounced and are displaced 20-30 °C upward in temperature, which is typical when the heating rate increases due to the thermal inertia of the material. In heating rate β = 30 °C/min (in): At the highest heating rate, all processes shift even more towards high temperatures. Moisture removal is observed at about 140-150 °C. The main destruction of humic acid occurs in the range of 280-600 °C. Peaks on the DSC curve become sharper and more intense, which is associated with less ability of the material for thermal equilibrium. The possible appearance of a second weak exothermic peak is associated with additional processes of re-combination or carbonization of the material. In general, the characteristic is shown as the heating rate increases, the temperatures of the beginning of the dehydration and destruction processes shift upward. Thermal effect peaks (DSCs) become more pronounced and shift to higher temperatures. The percentage of residual mass after 700-800 °C remains approximately the same, which indicates the stability of the final carbon residue (Table 5).

At a low heating rate (10 °C/min), the processes are smoother, a good separation of dehydration and decomposition is visible. At an average heating rate (20 °C/min), processes are accelerated, but details of individual degradation steps are lost. At a high heating rate (30 °C/min), the processes shift higher in temperature, the peaks become sharper due to insufficient thermal equilibrium (Table 2).

Scheme of TG/DSC peak displacement with increasing velocity Fig. 9.

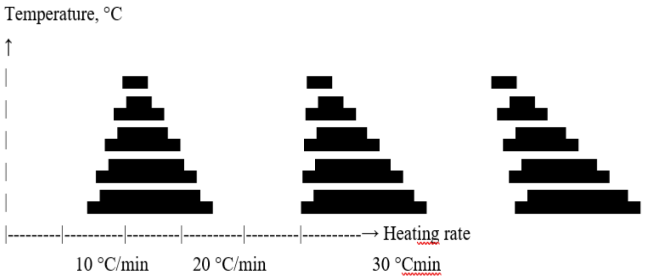


Fig. 9: Scheme of TG/DSC peak displacement with increasing velocity.

In this way (the faster the heating, the higher the peaks and the shift to the high temperature region), with an increase in the heating rate, the processes are mixed to higher temperatures. Peaks on the DSC become sharper and more intense. The residual weight is practically unchanged (~ 45-50%).

Determination of chemical composition of humic product. Further, using the element analyzer CHNS-O UNICUBE (Elementar Analysensysteme GmbH), the contents of carbon (C), hydrogen (H), nitrogen (N), sulfur (S) and oxygen (O) in humic acids (HA) obtained from brown coal of the Kuznetsky deposits were determined. The study was conducted to determine the elemental composition of these acids, which makes it possible to assess their chemical properties and potential applications in agriculture.

In humic acid from the Kuznetsk deposit, the carbon content is 49.605%. This may indicate a higher degree of aromaticity or polymerization of organic material in Kuznetsk coals. Hydrogen is present in acids from the Kuznetsk deposit: 3.071%. Nitrogen concentration: 0.93% in humic acid from Kuznetsk field. A higher nitrogen content may indicate the presence of more amino groups or proteins in the sample. In the Kuznetsk sample, the sulfur content is 0.391%. The high sulfur concentration may be related to the content of sulfide or organic sulfur compounds. Kuznetsk acid has a higher oxygen content of 45.263%. High oxygen content may indicate the presence of carboxyl groups, which increases the acidity and reactivity of the substance.

As a result of the experiments, humic acids were extracted from coal samples from the Kumyskuduk and Kuznetsk deposits by alkaline hydrolysis. From the coals of the Kuznetsk deposit weighing 10 g, 0.7 g of humic acids were obtained (yield 7%). Control drying is carried out alternately on two scales until the mass difference does not exceed 0.001 g. Taking into account the mass of the bag and filter, determine the mass of the precipitate.

Alkali concentration parameters ranging from 1 to 4%, temperatures ranging from 20 to 80°C, and reaction times ranging from 30 to 120 minutes were determined to be optimal for the complete extraction of HA from coal.

Further, microstructural analysis of coal revealed significant improvements in its physicochemical properties after sonication: the surface and structure were enriched with various oxygen-containing functional groups; coal ash content decreased to 3-5%. Ultrasonic treatment affected the pore structure, particle sizes and shapes, thus affecting the sorption activity of coal. During ultrasonic treatment of coal on the surface, the content of acid groups increases depending on the UST time (Table 6).

IR spectroscopic analysis revealed absorption peaks in the range of 1445-1400 cm^{-1} in the sonicated coal, which is consistent with bond fluctuations in oxygen-containing groups, primarily -OH and -COH deformations. The absorption band at 1620 cm^{-1} indicates the presence of both aromatic hydrocarbons and oxygen-containing C = O groups. Sonication of coal for more than 40 minutes is impractical, since the number of pores and the specific surface area decrease with longer treatment.

The physicochemical properties of the native and modified coals are shown in Table 7.

Table 6: Content of oxygen-containing groups in coal samples.

Coal sample	UST, min	Content of functional groups, mg-eq/g		
		total	carboxyl	phenolic
1	–	3.22	1.06	2.16
2	20	4.20	1.60	2.60
3	40	4.50	2.00	2.50
4	60	4.90	2.50	2.40

Table 7: Physical and chemical properties of Kuznetsk coal oxidation samples.

Sample	UST, min	Wa, %	Ad, %	Sample density, g/cm^3		
				bulk	seeming	True
1	–	10.80	12.56	0.771	1.160	0.443
2	20	11.27	3.27	0.642	0.283	0.020
3	40	17.39	5.50	0.500	0.275	0.062
4	60	16.00	4.18	0.622	0.257	0.037

In this work, to activate humate-containing substances and increase the yield of humic compounds, along with chemical and cavitation dispersion methods, the technology of hydraulic pulse discharge was used.

The method of electro-hydraulic pulse charge was chosen as a method with high efficiency due to the conversion of electrical energy into mechanical energy without the help of intermediate mechanical links.

In the brown coal samples of the Kuznetsk deposit (Fig. 10), the main elements were identified, such as silicon (Si), magnesium (Mg), calcium (Ca), boron (B), strontium (Sr), as well as metals, including aluminum (Al), iron (Fe), titanium (Ti) and nickel (Ni). It is important to note that the content of boric acid in ash samples in a ratio of 1:1 with ash allows to compensate for the friability of the ash particle and increase the measurement accuracy. This was confirmed in the preparation of tablets for analysis, where boric acid helped to obtain a homogeneous mixture and improve the results.

The content of silicon and magnesium in TPP-1 coal and ash samples (Fig. 11) indicates their significant role in the

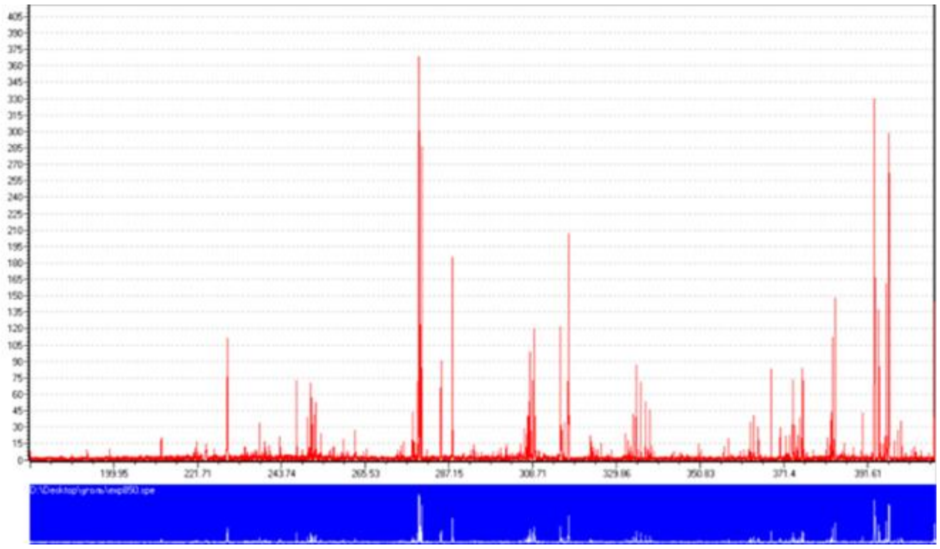


Fig. 10: Spectrum of coal sample from the Kuznetsk deposit

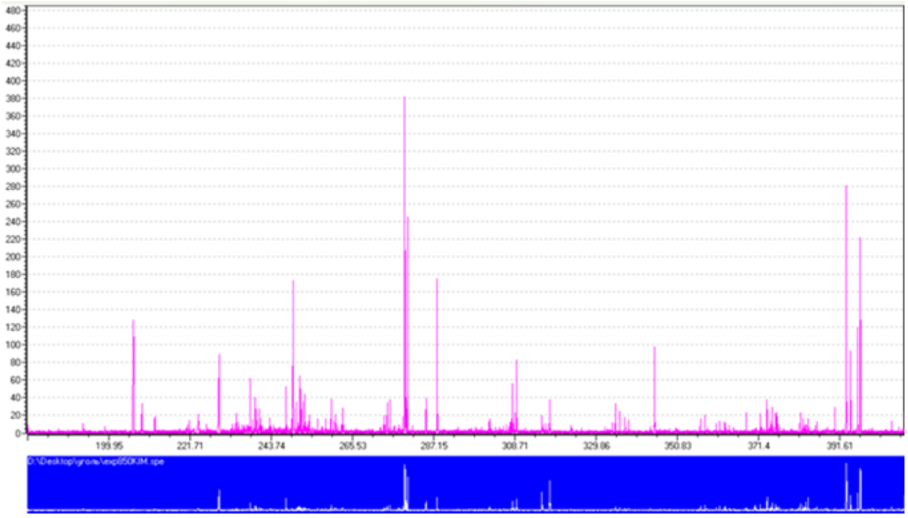


Fig. 11: Spectrum of ash sample.

chemical composition, and calcium and strontium are found in minimal quantities, which is probably due to natural calcium. Traces of iron and titanium confirm the presence of these elements in materials, and also indicate their possible role in technological processes associated with coal and ash. Nickel and aluminum in the ashes occur in small amounts, which is also consistent with the nature of these samples, usually containing low levels of such metals.

The atomic emission spectrometer results demonstrate the presence of a wide range of chemical elements in TPP-1 coal and ash samples, which confirms their multicomponent nature. These data are important for further studies aimed at assessing the impact of such elements on environmental processes, as well as their possible use.

The qualitative and quantitative composition of the organic substances that make up the humic acids isolated from the coals of the Kuznetsk field was determined using an Agilent gas chromatograph 7890A an Agilent 5975C mass-selective detector. Chromatomass spectrum of humic acids from Kuznetsk coals is shown in Fig. 12.

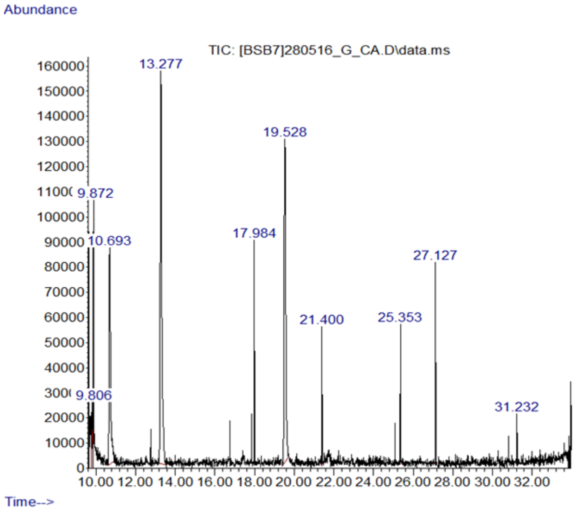


Fig. 12: Chromatomass spectrum of humic acids from the Kuznetsk coals.

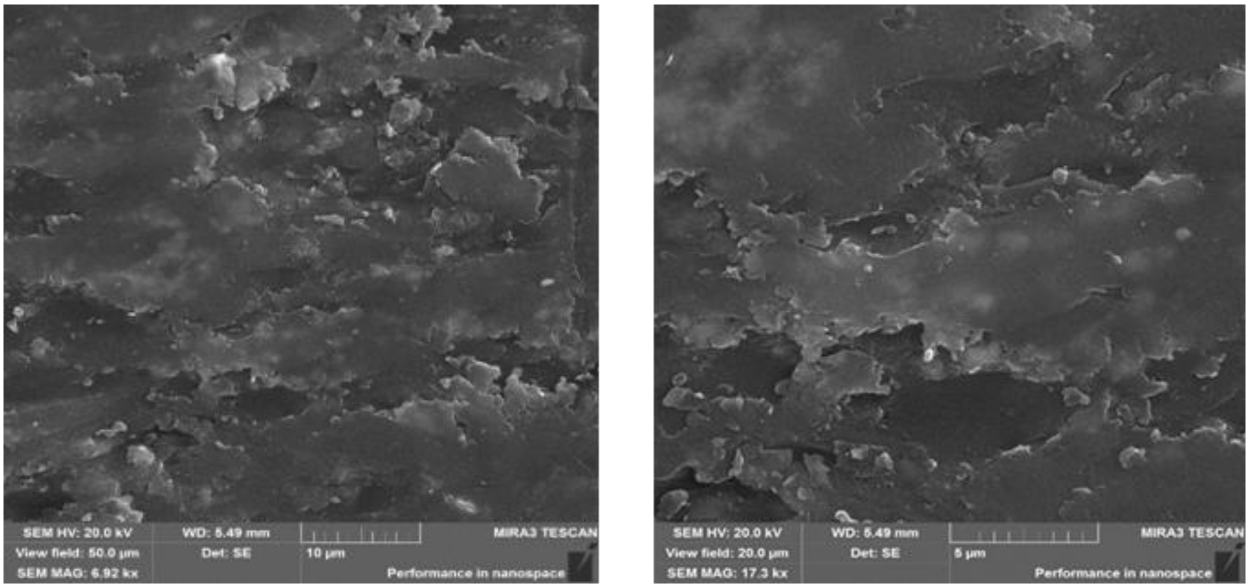


Fig. 13: SEM images of surface morphology of coals of Kuznetsk deposit.

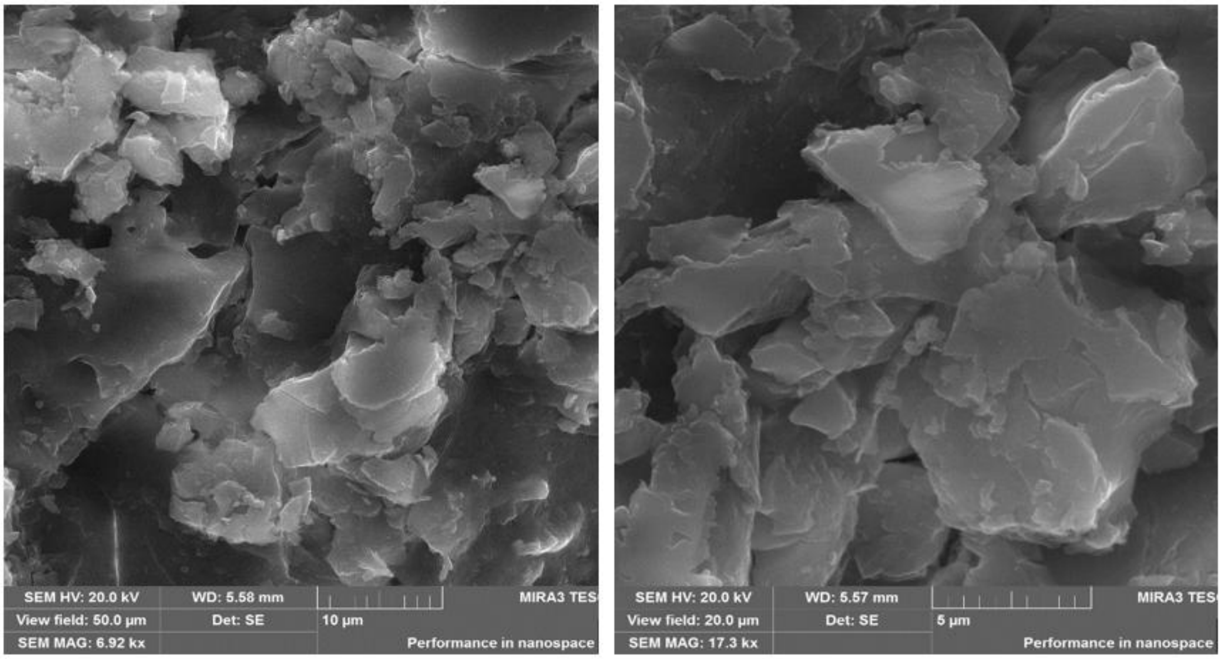


Fig. 14: SEM images of surface morphology of humic acids isolated from coals of Kuznetsk deposit.

As follows from Fig. 12 in the composition of humic acids, the identified individual compounds include: phenol, butylbenzene, 1,4-diethylbenzene, cis- and trans-decalin, 1,2,4,5-tetramethylbenzene, m- and p-cresols, tetralin, naphthalene, hexylbenzene, thymol, 2-methylnaphthalene, n-alkanes: C_{11}, C_{12} and C_{13}.

The surface morphology of the coal sample from the Kuznetsk deposit is characterized by the presence of finely dispersed pores and particles at the nanometer level (Fig. 13-14). Small pores with a diameter of about 5 nanometers are observed on the surface of coal, which indicates its microporous structure. Such pores play an important role in the adsorption properties of coal, since they are able to effectively capture and retain molecules of various substances, including gases and liquids. In addition, individual particles of about 1 nanometer are visible on the surface of the coal. These particles can be fragments of organic matter preserved during the formation of coal, or products of the interaction of coal with minerals. Nanoparticles of this size can also affect the reactivity of coal.

The morphology of humic acids obtained from the coals of the Kuznetsk deposit demonstrates a complex and heterogeneous structure with characteristic formations in the form of petals (Fig. 14).

Such petal-like structures consist of thin and elongated plate-like elements that overlap to form a layered and loose texture. This morphological feature provides a large specific surface area, which contributes to the high sorption and

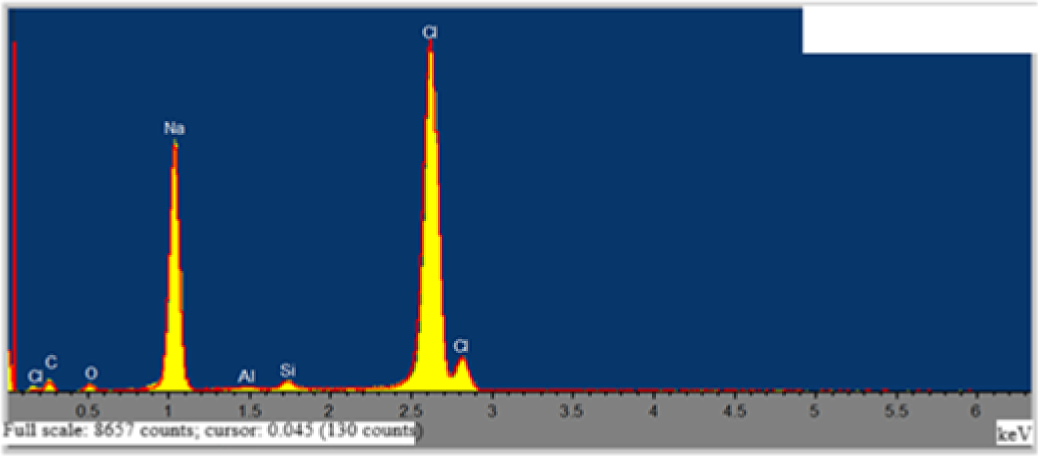


Fig. 15: Energy dispersive X-ray fluorescence spectrum of humic acid from Kuznetsk deposit.

Table 8: Elemental composition of isolated humic acids.

Sample: KUZ/HA

All results in weight%

Spectrum	C	O	Na	Al	Si	Cl	Итог
Spectrum 1	19.52	4.31	27.66	0.37	0.79	47.35	100.00
Spectrum 2	16.45	1.16	29.82	0.20	0.27	52.10	100.00
Spectrum 3	24.07	4.36	27.56	0.32	0.76	42.93	100.00
Average	20.01	3.28	28.34	0.30	0.61	47.46	100.00

reaction properties of humic acids. These formations can result from the specific molecular organization of humic substances due to their high content of aromatic and carboxyl groups. The heterogeneity of the structure is also manifested in the presence of micropores and pores of different sizes scattered on the surface of humic acids. Such pores, as a rule, contribute to the adsorption of various ions and molecules, which makes humic acids effective natural sorbents.

As a result of the study of paragraph 1.1, using various physicochemical analysis methods, the contents of carbon, hydrogen, nitrogen and other elements in brown coals, ash and TPP waste were determined, functional carbon-containing groups were identified using IR, PMR and chromatomass spectroscopic methods. A qualitative elemental analysis of coals and ash for the content of metals and non-metals was carried out at the atomic emission spectrometer. Ash content, coal humidity, volatile substance yield were determined, the influence of ultrasound on physical and chemical properties and formation of coal porous structure were studied. Ultrasonic activation allows you to change the pore structure, particle size and shape, and also affects the sorption activity of coal. To establish the optimal addition of the oxidizing reagent, experiments were carried out on the mechanochemical activation of brown coals.

Thermogravimetric analyses were performed to evaluate the thermal stability of the test samples and study the process of their decomposition under heat. The effect of UV radiation on samples of coals of various origins was studied in order to assess their resistance to photodegradation and changes in physical properties.

Optimization of the existing technology for the extraction of humic acids from coal was carried out. It was found that the most complete separation of sodium humates occurs during extraction with a 4% alkali solution at a temperature of 80 °C. The optimal reaction time is 120 minutes. To activate humate-containing substances and increase the yield of humic compounds, along with chemical and cavitation dispersion methods, the technology of hydraulic pulse discharge was used. The quantitative yield of humic substances relative to the initial amount of coal waste was calculated, the content of humic substances in the obtained products was estimated using spectroscopic methods.

Using a scanning electron microscope, pore sizes and volumes were determined, the morphology of humic acids obtained from coal was studied. The structural characteristics of the humic product and its solubility in various media were investigated.

The elemental composition of the isolated humic acids was analyzed via XRF spectroscopy, as presented in Fig. 15 and Table 8. The carbon content varied with the increasing

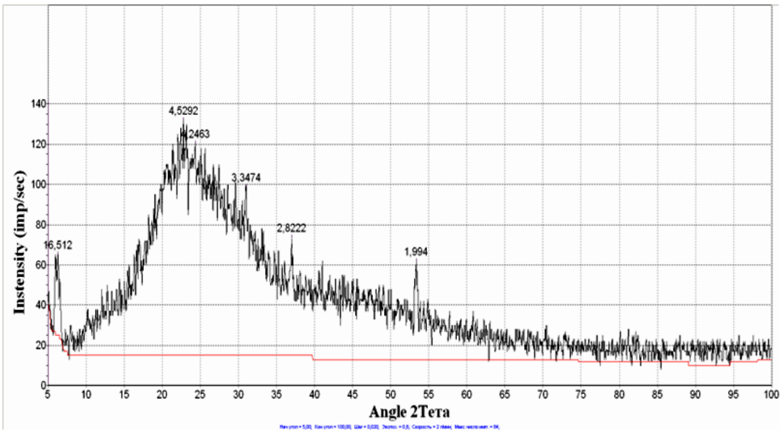


Fig. 16: X-ray diffractogram of humic acid from the Kuznetsk deposit.

concentration of the precipitated acid, alongside a potential increase in chlorine levels. The presence of sodium, as quantified in Table 7, confirms the use of an alkaline solution in extracting humates from coal mining waste, with the presence of silicate and aluminate compounds, including kaolinite. (based on Fig. 16). Chlorine, carbon, oxygen, aluminum, sodium and silicon found in small quantities.

NaCl – Halite (PDF Card No.: 00-075-0306); Reflexes: 3.25, 2.82, 1.99, 1.70, 1.62, 1.41, 1.26 Å; Cl_2 – dichlorine (PDF Card No.: 00-072-1642) Reflexes: 4.09, 3.34, 3.15, 2.72, 2.16, 2.04, 1.85, 1.78, 1.73, 1.72, 1.71, 1.52 Å; $NaClO_3$ – Sodium Chlorate (PDF Card No.: 00-075-1530) Reflexes: 3.78, 2.93, 2.67, 2.31, 2.18, 2.07, 1.97, 1.50, 1.33, 1.26 Å

Semi-quantitative results: Halite – 56%; Dichlorine – 20%; Sodium Chlorate – 24%.

Based on the results of elemental analysis, it can be concluded that humic acid from the Kuznetsk deposit contains more carbon, nitrogen and sulfur, which may indicate its more complex structure and potentially other properties.

- high carbon content (49.605%): Carbon forms the basis of the organic part of humic acids. A high carbon concentration indicates a more pronounced aromaticity and degree of polymerization, which contributes to the stability of the organic phase of meliorants in soil conditions. Such a structure of humic acids contributes to a long-term improvement in the structure of the soil and an increase in its fertility;

- high nitrogen content (0.93%): Nitrogen is an important element in plant nutrition, and its high content in humic acids from the Kuznetsk deposit increases their value in the production of organomineral fertilizers and meliorants. Nitrogen promotes accelerated plant growth and improves soil agrochemical properties

- sulphur content (0.391%): Although increased sulphur content may be undesirable for some specific applications, in the case of organomineral meliorants this is an advantage. Sulfur is involved in the synthesis of plant-important amino acids and enzymes, which can contribute to improving their nutrition.

This work considers the extraction and comprehensive characterization of humic acid (HA) obtained from brown coal of the Kuznetsk deposit, comparing the main indicators with the data of modern studies of 2024-2025. The comparison was carried out by product yield, ash content, functional composition (-COOH/-PhOH), degree of aromaticity, molecular weight characteristics, thermal stability, as well as sorption-complexing and agronomic indicators.

Overall, HA obtained show: 1) comparable or higher yields with reduced ash content; 2) an increased proportion of carboxyl groups against the background of a moderate phenolic component; 3) a higher proportion of aromatic carbon according to ^{13}C-NMR data and a lower E4/E6 ratio; 4) moderate polydispersity (PDI) and weight average molecular weight in the range characteristic of lignite HA;4) higher temperatures of the onset of thermal destruction and a large proportion of slowly oxidizable domains by TG/DSC.

Together, these results indicate the structural and functional advantages of Kuznetsk HA and explain their increased efficiency in remediation/agrotechnology applications.

Thus, the humic acid from the Kuznetsk deposit, due to the high content of carbon, nitrogen and sulfur, has a more balanced elemental composition, which makes it promising for use as a component of organomineral meliorants. It is able to effectively improve the physicochemical properties of the soil and provide plants with the necessary nutrients.

4.Conclusion

Studies of the characteristics of brown coal at the Kuznetsk deposit made it possible to obtain a significant idea of its physicochemical properties, which contributed to a reasonable assessment of its potential use in various industries. Critical indicators such as ash content, humidity and volatile matter yield confirm the suitability of this coal for energy and industrial purposes. The results of the analysis show that Kuznetsk brown coal is characterized by low ash content and high yield of volatile components, which makes it an attractive candidate for thermal processing, including gasification and pyrolysis. In addition, these characteristics highlight its significant potential as a source of raw materials for the chemical industry, especially in the production of synthetic gases and liquid hydrocarbons. The results of the study, based on the application of elemental analysis and a number of spectroscopic methods, including infrared (IR) and thermogravimetric analysis (TGA), made it possible to obtain valuable data on the chemical composition and structural characteristics of coal, facilitating identification. key functional groups and quantitative assessment of the main components. The data obtained are essential for assessing the industrial potential of the Kuznetsk brown coal deposit.

As a result of the experiments, humic acids were extracted from coal samples from the Kuznetsk deposits by alkaline hydrolysis. The obtained humic acid samples were analyzed by elemental analysis, IR and TG/DSC analysis. As a result of the study of the properties of humic acids obtained from brown coal of the Kuznetsk deposit, important data were obtained on the composition and characteristics of these organic compounds. Humic acids, as an important part of the organic mass of coal, demonstrate a wide range of useful properties that can be used in various industries, such as agriculture, ecology and medicine.

Extraction of humic acids from brown coal using a 4% NaOH solution at 80°C for 2 hours showed optimal conditions for the production of humic acids, with a yield of 7% for the coals of the Kuznetsk deposit. Ultrasonic treatment improved the physicochemical properties of coal, increasing the content of oxygen-containing groups, which was confirmed by IR spectroscopy.

A study of the composition of functional groups in humic substances and coal ash using infrared spectroscopy and nuclear magnetic resonance showed the presence of various functional groups, such as carboxyl, phenolic and hydroxyl groups, which is confirmed by characteristic absorption bands in the IR spectra. In the range of 3800-3550 cm^{-1}, hydroxyl groups were detected, while the ranges of 1600-1250 cm^{-1} indicated aromatic structures, which indicates a high content of carbon bonds. Also, IR spectra of humic acids showed the presence of carboxyl and aromatic groups, which is confirmed by their significant role in the structure of these substances. NMR spectra for humic acids confirmed a high degree of aromaticity and complex aliphatic substituents in the structure of coal extracts. TG/DSC analyses showed a two-step degradation of humic acids with the release of volatile components and carbon residues at high temperature.

Studying the structure and shape of particles of humic substances and coal ash using microscopy made it possible to identify key morphological features of the studied samples. Coal from the Kuznetsk deposit exhibits a microporous structure with pores with a diameter of about 5 nanometers, which indicates the high adsorption capacity of coal, especially with regard to gases and liquids. Nanoparticles, about 1 nanometer in size, can be products of organic decomposition or interaction of coal with minerals, which can also have an impact on the reactivity of coal.

The morphology of humic acids isolated from the coals of the Kuznetsk deposit is characterized by a complex and heterogeneous structure with petal-like formations. These structures consist of thin plate elements overlapping each other, which creates a layered and loose texture with a large specific surface. This, in turn, contributes to the high sorption and reaction properties of humic acids. The presence of micropores of different sizes on the surface of humic acids enhances their ability to adsorb ionized molecules and other substances, which makes them effective natural sorbents.

The main results of the study showed that the humic acids of brown coal of the Kuznetsk deposit are highly reactive due to the presence of functional groups such as carboxylic and phenolic. These groups determine the acidity of humic acids, their ability to complex and sorb heavy metals, which makes them promising for use in agrochemical and environmental technologies. Thus, the results of the study indicate a high potential of humic acids obtained from brown coal of the Kuznetsk deposit for their further use as environmentally friendly additives and sorbents, as well as effective components to increase soil fertility. In the future, it is advisable to continue research to expand the areas of their use and improve the methods of their extraction and processing.

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Conflict of Interest

There is no conflict of interest.

Supporting Information

Not applicable.

CRediT Statement

A. P. Nauanova: Investigation, Data curation, Visualization and Validation, **S. Tyanakh:** Formal analysis, Validation, Writing - Original draft, Writing - Review & editing, **T. O. Khamitova:** Conceptualization, Methodology, Investigation, Resources, Supervision, Project administration and Funding acquisition, **N. Parmanbek:** Data curation, Investigation, Formal analysis and Software, **Fengyun Ma:** Investigation, Validation and Software, **A. Karimova:** Investigation, Data curation, Visualization, Validation.

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