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# VALORIZATION OF LIGNITE USE IN "GREEN" TECHNOLOGIES: A REVIEW

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**Abstract.** The increased utilization of lignite in "green" technologies represents a critical step toward the rational use and valorization of low-grade fossil fuels. This study examines the current state of lignite deposits in Ukraine and explores its potential applications in non-energy and environmentally sustainable energy sectors. The chemical composition of humic acids derived from brown coal was analyzed, along with their ability to undergo hybrid modification with biodegradable materials such as hydrogels, biofilms, and composites. The potential of lignite-based humic acids as sorbents for the removal of heavy metals from wastewater was evaluated, highlighting their role in ecological remediation. Special attention was given to the process of low-temperature gasification of lignite for the production of additives to polymer-modified bitumen. The results confirm the feasibility of developing innovative lignite processing methods in accordance with the principles of "green" technologies.

**Keywords:** lignite, valorization, green technologies, humic acids, biodegradable polymers, sustainable materials, lignite gasification

## 1. Analysis of the Current State of "Green" Technologies for the Use of Lignite Raw Materials in Ukraine

To initially determine the potential of Ukraine's raw material base for developing areas of lignite use in "green" technologies, we analyzed the existing lignite deposits and the degree of their industrial utilization.

It is well known that Ukraine is a country with a developed raw material base of lignite, the wealth of which is due to the peculiarities of the geological structure of its territory.[1] On the territory of Ukraine, lignite deposits are located in the geological structures of the Dnipro Basin (Ukrainian crystalline shield), Dnipro-Donetsk Depression, Prydnestrove coal-bearing area (Volyno-Podilska plate, Carpathian Deflection and Zakarpattia coal-bearing areas, Lower-Dniester plane (Depressions in Neogene sediments) (Fig. 1). The total balance sheet reserves of lignite in Ukraine amount to about 2.9 billion tons. The largest explored deposits are concentrated in three regions: Dnipro region (1,32 billion tons), Kirovograd region (750 million tons), and Kharkiv region (389 million tons). Geologically, the fields are located in different regions: Dnipro-Donets Basin, Ukrainian Shield and Trans-Carpathian Intermountain Depression, which defines specific production conditions depending on geological characteristics. In general, it can be noted that as of January 01, 2024, the total number of lignite deposits in Ukraine reaches 80, but only 3 of them are actively developed[2]. The distribution of lignite reserves by regions of Ukraine as of 01.01.2024 is shown in Table 1.

Analyzing the data presented in Table 1, it can be concluded that the largest deposits of lignite of *A+B+C1* categories in Ukraine are located in Dnipro region (1320644.00 thousand tons), Kirovohrad region (750833.00 thousand tons) and Kharkiv region (389985.00 thousand tons).[2]

The distribution of deposits by the degree of commercial development as of January 1, 2024, is shown in Table 2.[2] Based on the data presented in Table 1.2, there are only 3 operating fields in Ukraine with balance reserves of *A+B+C1* categories equal to 9331 thousand tons.The current state of lignite mining in Ukraine also shows that only 3 areas of the Morozivske deposit in the Dnipro lignite basin are producing lignite, just in small quantities it is used to produce valuable chemicals such as montane wax and humates, while its potential raw material role is relevant to many sectors of modern industry: medicine, agriculture, infrastructure construction, environmental management, *etc*. Lignite in Ukraine is

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classified according to DSTU 3472:2015, and international standards ISO 11760:2005 and ASTM D388-12. DSTU 3472:2015 regulates parameters such as volatile content and calorific value in detail but does not take into account modern environmental aspects. International standards provide a broader classification but can be difficult to fully integrate into internal processes due to differences in metrology systems.

Fig. 1 shows data on lignite production in Ukraine in the period from 2011 to 2024.[2]

**Table 1.** Distribution of lignite reserves by regions of Ukraine as of 01.01.2024 [2]

| Region. | Carrying reserves, thousand tons | | Number of deposits |
|---|---|---|---|
| | *A+B+C1* | *C2* | |
| Dnipro, including: | 1320644.00 | 258053.00 | 21 |
| Dnipro Basin | 1033945.00 | 258053.00 | 18 |
| Donets Basin | 286699.00 | 0.00 | 3 |
| Zhytomyr | 10884.00 | 0.00 | 2 |
| Zakarpattia | 38745.00 | 0.00 | 4 |
| Kirovohrad | 750833.00 | 39604.00 | 44 |
| Kharkiv | 389985.00 | 0.00 | 1 |
| Cherkasy | 82225.00 | 1524.00 | 8 |
| **Total:** | 2593316.00 | 299181.00 | 80 |

**Table 2.** Distribution of deposits by the degree of industrial development

| Degree of industrial development | Number of deposits | Carrying reserves, thousand tons | |
|---|---|---|---|
| | | *A+B+C1* | *C2* |
| Free areas near the operating sections | 1 | 784.00 | 0.00 |
| Free areas near the operating mines | 8 | 48869.00 | 0.00 |
| Areas to be explored | 1 | 6285.00 | 2169.00 |
| Operating sections | 3 | 9331.00 | 0.00 |
| Closed sections | 8 | 87887.00 | 307.00 |
| Closed mines | 7 | 87463.00 | 2022.00 |
| Promising exploration areas for sections | 7 | 61766.00 | 849.00 |
| Promising exploration areas for mines | 25 | 1196315.00 | 285095.00 |
| Group A reserve areas for sections | 9 | 716944.00 | 0.00 |
| Group A reserve areas for mines | 6 | 338699.00 | 8739.00 |
| Group B reserve areas for sections | 4 | 31512.00 | 0.00 |
| Group B reserve areas for mines | 1 | 7461.00 | 0.00 |
| **Total:** | 80 | 2593316.00 | 299181.00 |

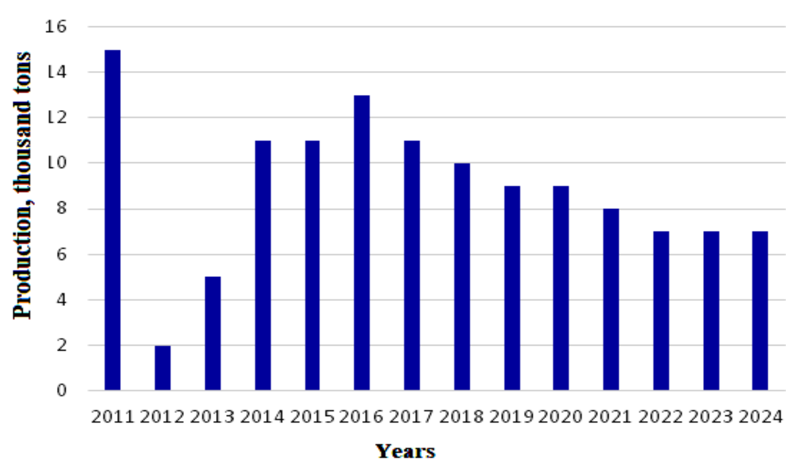



**Fig. 1.** Lignite production in Ukraine from 2011 to 2024

Over the period 2011-2024, lignite production decreased by more than 20 %, and there are currently only three operating open-pit mines at the Morozivske deposit in the Dnipro lignite basin.

Today, lignite processing in Ukraine includes three main areas:[4]

- technologies aimed at improving the quality of coal products to meet the needs of thermal power plants and household consumers, as well as the cement and metallurgical industries by improving the quality characteristics of processed products (beneficiation and briquetting, pulverized coal and water-coal fuel). The essence of these technologies is that there are no changes at the molecular level in coal processing. The macromolecule of coal is not subject to destruction, and the transformation occurs due to changes in some of the physical properties of coal. According to Ukrainian mining companies, these technologies are used for 75% of lignite produced;
- technologies that provide products with new consumer characteristics, allowing the production of refined products with a completely different price range by thermal treatment (coking, semi-coking, gasification, and production of synthesis gas derivatives - methanol, ammonia, motor fuel, *etc*., as well as hydrogenation). This type of technology is based on the achievability of different degrees of destruction of organic matter during its transformation. The destruction of molecules occurs through the physical impact of coal on the organic mass. At first, it starts with labile bonds and then along the carbon-carbon line. Semi-coking and coking combine the irreversible processes of decomposition of a heated substance with the release of low molecular weight products and condensation to form solid high-carbon substances. Unlike coking processes, gasification involves the complete destruction of organic matter. Gasification products CO and $H_2$ can be used for the synthesis of various organic compounds. According to Ukrainian mining companies, these technologies are used for 20% of the lignite produced.
- non-fuel technologies aimed at producing rock wax, humane drugs, adsorbents, and valuable derivatives in the form of polymers, humic substances, *etc*. These technologies are based on the ability to separate various components from coal substances depending on their solubility in different solvents and thus produce substances that have non-fuel applications. For today's Ukraine, this applies mainly to the production of rock wax. According to the data of Ukrainian mining enterprises, these technologies are used for 2% of lignite production.

Given the fact that lignite production in Ukraine ranged from 2 to 15 thousand tons per year from 2011 to 2020, and the forecasted potential of coal production by lignite enterprises for the period up to 2047 is about 24.000 tons per year,[1,4] the search and development of non-energy methods of lignite's use is a very promising scientific and practical task (Fig. 2). Thus, it is important to note that the analysis of deposits, quality indicators, current processing directions, and potential of lignite production in Ukraine shows that only 2% of modern lignite is processed within the framework of "green" technologies of use and processing to obtain useful substances and materials.

At the same time, the "green" and non-fuel use of lignite is one of the most promising areas of development within the framework of the implementation of the Low Carbon Development Strategy of Ukraine until 2050, as it allows to obtain marketable products in high demand, the cost of which is much higher than the cost of raw materials.

This area is also fully in line with the European Green Deal, adopted in 2019 by the European Commission as part of the EU's goal of achieving climate neutrality by 2050, which Ukraine joined in 2021. All of this leads to the conclusion that it is necessary to search for and develop non-energy methods of using lignite, which is a very promising scientific and practical task in the development of industrial technologies for the rational "green" use of lignite resources to obtain new and modify existing materials. The analysis of the existing lignite deposits in Ukraine and the degree of their industrial utilization indicates the presence of significant reserves of lignite as a source of humic acids but their extraction is carried out at a very low level without realizing the small potential of the "green" use of lignite. It is worth emphasizing that, in turn, this is due to the lack of developed industrial technologies for the rational non-energy use of lignite resources in the form of humic acids to produce new materials and modify existing ones. Actually, lignite, due to its structure, natural sorption and ion-exchange properties, and the presence of a large amount of biologically active humic and acids, is of high value as a raw material for implementing the principles of the European Green Deal in the framework of processing into materials for technological, environmental, agricultural, household and other purposes.

The potential humic acid content in Ukrainian lignite was analyzed in the main regions to identify the deposits with the highest potential for efficient humic acid extraction.[5]

Table 3 shows the potential range of humic acid content in lignite mined in different regions of Ukraine.

Summarizing the results of the analysis of the potential content of humic acids in lignite in different regions of Ukraine, it should be noted that deposits in Dnipro region, in particular Verkhniodniprovskyi district, have the highest potential for humic acid production with a content of 19.03-41.32 % wt. per working sample. At the same time, Zakarpattia deposits are also rich in organic matter, which allows them to be used as a source of humic acids, especially for the agricultural sector.

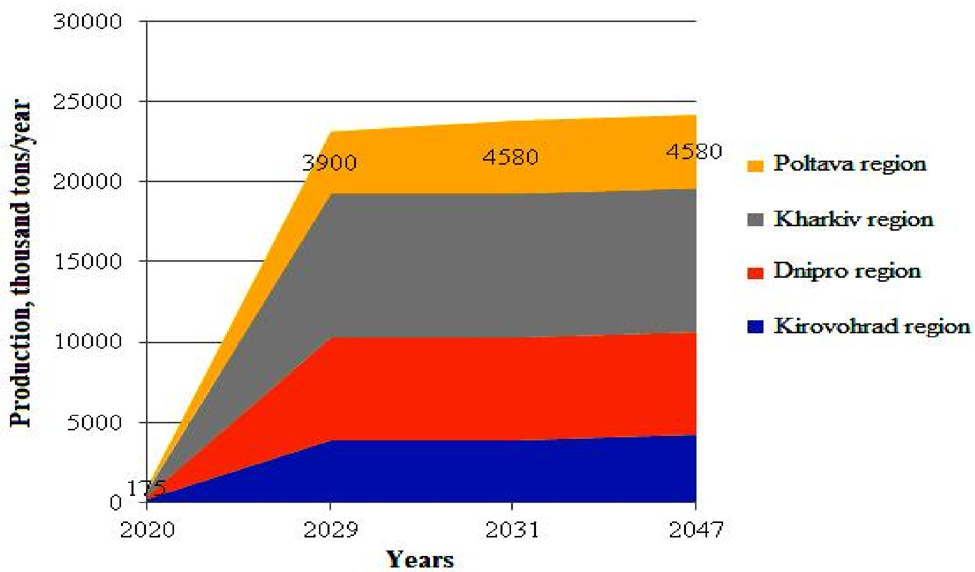



**Fig. 2.** Coal production potential of the lignite complex enterprises for the period up to 2047

**Table 3.** Range of humic acid content in lignite by region of Ukraine [5]

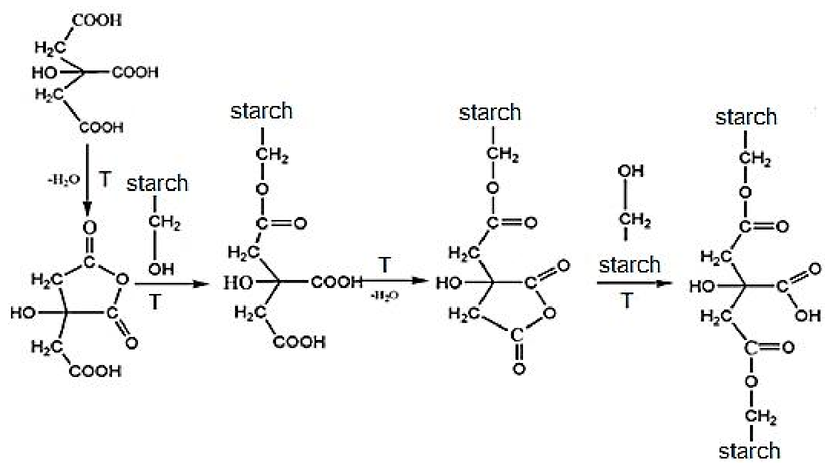
| Region | $HA^r$, wt.% | $HA^a$, wt.% | $HA^{af}$, wt.% | $HA^{daf}$, wt.% |
|---|---|---|---|---|
| Dnipro | 19.0-41.4 | 35.4-49.5 | 44.0-55.6 | 51.2-74.6 |
| Zhytomyr | 20.9-27.9 | 35.8-38,0 | 45.9-49.2 | 52.9-62.0 |
| Zakarpattia | 24.6-27.8 | 35.7-37.9 | 45.9-49.2 | 52.9-62.0 |
| Kirovohrad | 16.7-25.6 | 34.1-40.1 | 40.9-48.5 | 47.4-62.7 |
| Kharkiv | 20.8-24.2 | 32.5-41.0 | 45.0-47.2 | 52.6-56.7 |
| Cherkasy | 16.0-22.6 | 31.2-42.0 | 43.2-48.8 | 46.1-58.6 |

The deposits with the highest yield of humic acids per working sample include the Petrykivka geological and industrial region, Dnipro region, Dnipro-Donetsk depression, and Pivdennyi board, where the yield of humic 142 acids is: for the deposit with the 204 passport – 40.76 % by weight, for the deposit with the 205 passport - 41.00 and 39.13 % by weight, and for the deposit with the 206 passport - 41.32, also 40.02 and 39.95 % by weight, what are the best values of rubber acids yield from lignite in Ukraine. If we consider the highest yield of humic acids per analytical sample, the general situation with the content of humic acids that can be obtained from Ukrainian lignite deposits is the same as with the working sample, namely, Petrykivka geological and industrial region, Dnipro region, Dnipro-Donetsk depression, Pivdennyi board deposit with passports 204, 205, 206, where the maximum yield is 48.18, 49.46, 49.43, respectively.

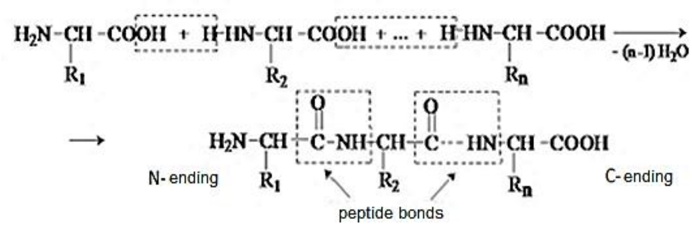
## 2. Development of "Green" Technologies for the Use of Lignite Humic Acids in the Modification of Biodegradable Polymeric Materials

The chemical composition of lignite humic acids proves that due to the presence of a large number of different functional groups in their composition, such humic coal derivatives have significant functionality as a hybrid modifier.[6-8] Among the oxygen-containing reactive groups expected to be found in lignite humic acids (carboxylic, hydroxyphenolic, hydroxyl, carbonyl, quinonic, ester, acetal, lactone, and ester), carboxylic and hydroxyphenolic are worthy of attention not only because of the significant level of presence but also due to their significant reactivity with a wide range of reactive groups of various biodegradable materials. Carboxyl groups bind to the corresponding ionic points of various groups of biodegradable materials:

- crosslinking by methylene hydroxyl groups (biodegradable polymers based on cellulose, starch, gelatin, *etc.*) with the formation of ester bonds:




– coordinated binding to amino groups of various biodegradable materials (gelatin, polycaprolactone, *etc.*), as in the case of -CONH- bonds (peptide groups):




The carboxyl groups of COO- humic acids of lignite are very valuable precisely because of the hybrid potential of HA, as they are the groups that impart the basic chemical properties of lignite humic acids and because they can form electrostatic bonds, although it is difficult to determine the points at which bonds are formed between the carboxyl groups of lignite humic acids and various biodegradable materials. Due to the structural complexity of lignite humic acids, it seems reasonable to assume that the bonds are formed by the bipolar attraction between them not only due to the polarity of the carboxyl group but also due to the molecular exchange of lignite humic acids. These bonds result, on the one hand, in a multitude of binding points, which ensures the stability of various biodegradable materials obtained as a result of interaction with lignite humic acids. It has been experimentally determined that in the anionic form, the carboxyl group has more resonant structures than in the unionized form. Therefore, it will usually be in the ionic form because it reacts more with various biodegradable materials.

If the structure containing the carboxyl group has double bonds, the number of resonant structures in the ionic form will be greater, and therefore the polarity and reactivity will also be greater.

When the conjugation between double bonds is preserved, which in lignite humic acids is preserved in the aromatic structure, and if the side chains and reactive side conjugated groups with the structure, these groups will be highly reactive.

The hydroxyphenolic -OH groups will have the backbone groups of a variety of biodegradable materials as the first opportunity for a hybrid reaction *via* electrostatic bonds. The hydroxyphenolic groups, which are not ionized (due to pH), will also have the opportunity to bind in a coordinated manner to the non-ionized peptide -CONH groups of various biodegradable materials and through the hydrogen bonds of the phenolic groups with the active groups.

Quinone groups are electron-accepting and are responsible for the production of reactive oxygen species. In the structure of the studied humic acids, they are reduced to semiquinones, which are stabilized by their aromatic rings and further reduced to hydroquinones, which are even more stable.[9]

The reaction of hydroxyl groups with various biodegradable materials is not as important as the reaction of phenolic and carboxyl groups. However, such a reaction is relevant when considering the reactivity between molecular aggregates and the possibility of determining modifications of reactive groups other than humic acids (aimed at obtaining other properties, for example, attachment of -O-$SO_3$H group).

Carbonyl groups do not have an important reactivity towards the peptide groups of various biodegradable materials. Nevertheless, due to the molecular aggregates formed between two macromolecules, these groups can be important in terms of polarity (even though it is low) and the number of groups, which, even if low relative to the main groups (carboxyl, phenolic, and hydroxyl) is much higher than that of the other groups present (quinone, ester, acetal, lactone and ester).

In compounds such as lignite humic acids, one of the most important properties of the molecular structure is polarity. Polarity significantly increases the reactivity of active peripheral groups. It is important to note the property of humic acids to dissolve in neutral or alkaline conditions. This property depends on the chemical composition of different humic acids and, accordingly, on their origin. A mechanism for the coordination of humic acid molecules depending on the conditions of their dissolution medium has been proposed – Fig. 3.[10]

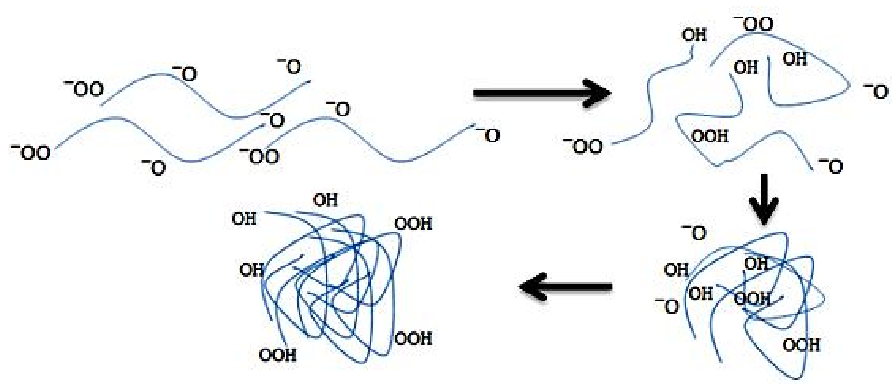



**Fig. 3.** Behavior of humic acid molecules in alkaline conditions and the process of their coordination of aggregation at a decrease in pH

The following stages of humic acid coordination occur depending on the change pH:

- alkaline pH: charge repulsion;
- pH reduction: intramolecular aggregation of humic acids;
- pH reduction: intermolecular aggregation of humic acids;
- acidic pH: precipitation of humic acids.

In alkaline environments, phenolic and carboxyl groups are deprotonated, and the repulsion of these negatively charged groups causes the molecules to adopt an extended configuration. At lower pH, the functional groups are protonated, and the repulsion effect is minimized, causing the humic acid molecule to adopt a folded and compact structure. At this stage, the hydrophobic parts of the humic acids are inside the structure, and the hydrophilic parts are in contact with the aqueous medium.

This behavior is responsible for the emulsification characteristics of humic acids, their micellar organization, and reduced surface tension. These humic acid molecules form aggregates at the intramolecular level, followed by intermolecular aggregation and, finally, precipitation. It has been experimentally established that pH is related not only to solubility but also to the stability of aqueous suspensions of humic acids.

A diffuse double electric layer forms around the charged particles, which protects them and allows the system to become discharged. Moreover, the ion concentration determines the charge protection of humic acid particles, which is greater for systems with lower ionic strength since ionic species will have a stronger interaction with the electric layer than with solvent molecules.

Since humic acids are weak polyelectrolytes, they can exist in water both as dissolved molecules and in dissociated form. This mechanism corresponds to the soluble fraction of humic acids. The insoluble fraction interacts with the environment through the surface and acts as an ion exchanger, releasing H+ ions into the solution, while anions remain insoluble.

This characterization of the soluble properties of humic acids indicates their high potential for hybrid modification of water-soluble polymers. Since most materials from such polymers are obtained under conditions of their dissolution in an aqueous medium, it looks very promising to carry out hybrid modification of humic acids by deprotonating their phenolic and carboxyl groups and being in the active form relative to the functional groups of polymers.

It has been experimentally established[11] that carboxyl and hydroxyphenolic groups predominate in humic acids, and carbonyl and hydroxyl groups are also present in significant amounts. The presence of phenolic hydroxyl -OH and carboxyl COO- groups in the amount of 2-4 wt. % determine the ability of coal humic substances to act as a hybrid modifier in relation to polymeric materials (biodegradable substances) due to the following mechanisms: chemical interaction with methylene hydroxyl groups to form ester bonds, coordination binding with amino groups to form peptide groups -CONH-, dipole-dipole interaction with the presence of hydrogen bonds and conformational changes. It was found that phenolic hydroxyl -OH and carboxyl COO- groups in the amount of 2-4 wt. % determine the ability of humic acids of coal to act as a hybrid modifier in relation to polymeric materials (biodegradable substances) due to the following mechanisms: chemical interaction with methylene hydroxyl groups with the formation of ester bonds, coordination binding with amino groups to form peptide groups -CONH-, dipole-dipole interaction with the presence of hydrogen bonds and conformational changes.

The conducted research made it possible to formulate the technological basis for the use of humic acids of lignite as hybrid modifiers of biodegradable materials, which, in turn, allows to form comprehensive technological approach to the creation of lignite processing schemes with the subsequent use of humic acids in the processes of obtaining hybrid materials: hydrogels, biofilms, composite materials, and coffee-filled composites.[12-14]

In general, two-stage technological schemes for the use of lignite humic acids as hybrid modifiers of biodegradable materials have been formalized. At the first stage of the technologies for the use of lignite humic acids to produce hybrid-modified biodegradable materials, humic acids are produced. At the second stage, they are hybridly modified with different types of biodegradable materials: hydrogels, biofilms, coffee-filled composites and composite materials.

In principle, the first stage of technologies for using lignite humic acids as hybrid modifiers of biodegradable materials includes producing humic acids from lignite by grinding it to obtain microparticles, preparing a suspension in a weak alkali solution, and extracting humic acids from the suspension in a mixing reactor from coal microparticles of humic acids (Fig. 4).

The first stage is a waste-free scheme for processing lignite into a wide range of products for technological, environmental, and economic purposes that are in high demand, including:

- crushed and granular sorbents (active carbons) for purification of process, domestic, and waste water from heavy metals, organic pollutants, water treatment for drinking water supply, purification of process gases, recovery of hydrocarbon vapors;

- humic acids as hybrid modifiers of biodegradable materials.

The liquid alkaline extract of humic acids is obtained by extracting crushed lignite with an aqueous alkali solution, followed by centrifugation. The solid residue of the centrifugation is used to obtain a granular sorbent. A part of the alkaline extract of humic acids is subjected to acid treatment and sent for filtration with subsequent drying to obtain solid polydisperse humic substances.

The production stage of humic acids, according to the presented technological scheme, is waste-free. The solid residue after coal extraction with alkali is used to make granular sorbents in the form of activated carbon.

The second stage of the technological process of using lignite humic acids as hybrid modifiers of biodegradable materials includes the production of hydrogels, biofilms, coffee-filled composites, and composite materials. Biodegradable gelatin hydrogels modified with humic acids were obtained with the following performance properties (Table 4).[12,15]

According to a certain set of performance properties, the biodegradable gelatin hydrogels obtained by hybrid modification with humic acids correspond to the most effective commercial hydrogels and are recommended for the preparation of antibacterial gels, masks for human skin, and the manufacture of patches for biologically active substances. Hybrid modification of biofilms based on polyvinyl alcohol with humic acids allows to obtain high-strength waterproof films with antibacterial properties for packaging wet and dry food and non-food products and products that correspond to the most effective commercial biodegradable packaging films (Table 5).[13,15]

Hybrid modification of biofilms based on hydroxypropyl methyl cellulose with humic acids allows to obtain durable water-soluble films with antibacterial properties for use as packaging for dry food products (bread, cereals, nuts, *etc.*) with an extended shelf life, which correspond to the most effective commercial biodegradable packaging films (Table 6).[16,17]

The hybrid modification of biodegradable composite and coffee-filled polylactide composites with humic acids allows, according to the achieved level of performance characteristics, to use them for the production of food containers and packaging, membranes and matrices for micro- and nanoelectronics - Table 7.[18,19]

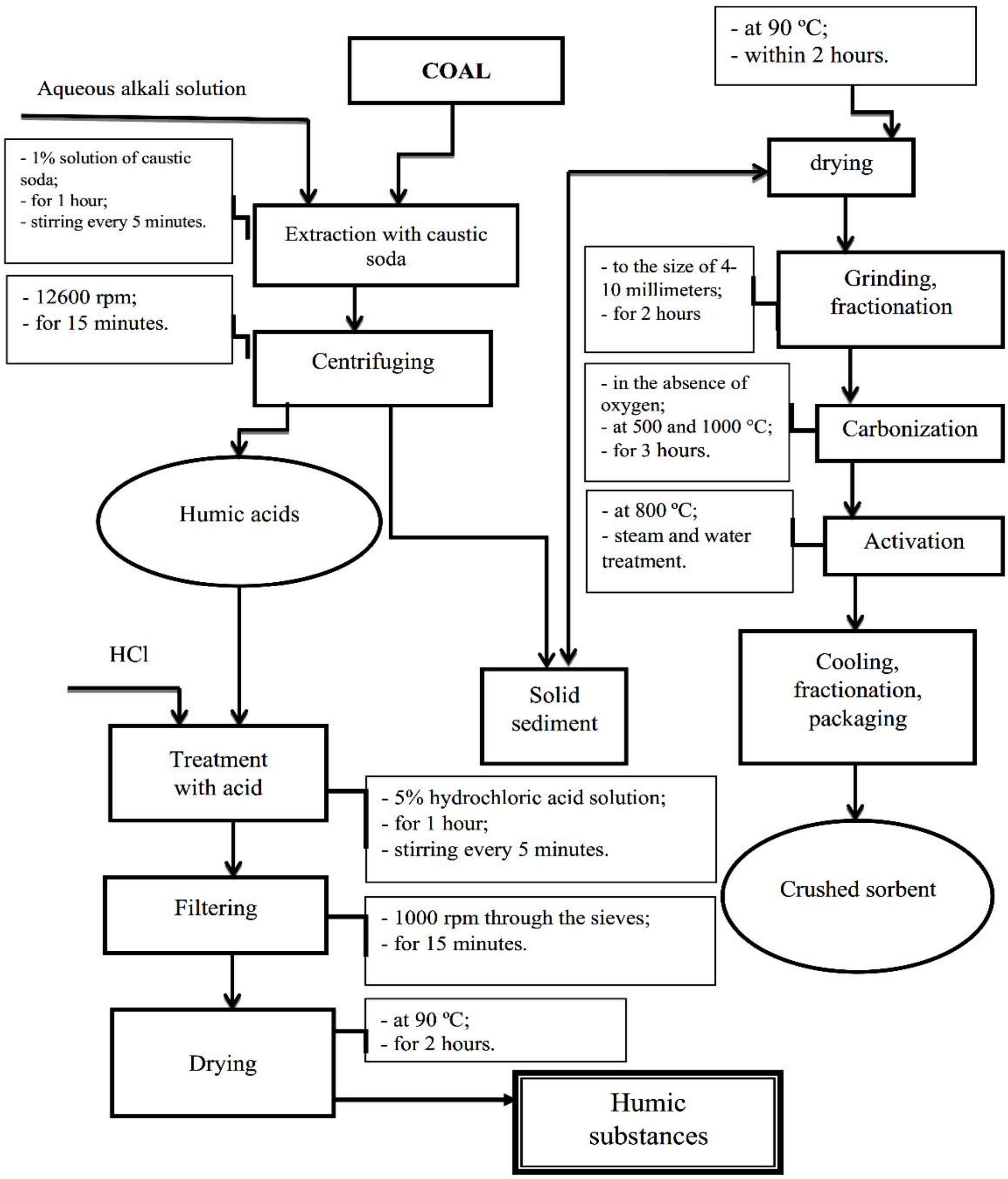



**Fig. 4.** Scheme of the first stage of technologies for the use of lignite humic acids as hybrid modifiers of biodegradable materials

**Table 4.** Properties of hybrid biodegradable gelatin hydrogels modified with humic acids

| Humic acid content, wt. % | Degree of swelling, wt. % | Time of mold appearance, hours | Time of stickiness loss, min. |
|---|---|---|---|
| 5 | 36.4 | > 900 | 7 |
| 10 | 29.7 | > 900 | 6 |
| 15 | 28.9 | > 900 | 4 |

**Table 5.** Performance properties of hybrid biodegradable films with bactericidal properties based on polyvinyl alcohol modified with humic acids

| Humic acid content, wt. % | Water absorption, wt. % | Tensile strength at break, MPa | Relative elongation at break, % | Time of mold appearance, hours |
|---|---|---|---|---|
| 5 | 170 | 25 | 24 | 168 |
| 10 | 160 | 27 | 25 | > 500 |
| 15 | 150 | 29 | 26 | > 500 |

**Table 6.** Performance properties of hybrid biodegradable films based on hydroxypropyl methyl cellulose modified with humic acids

| Humic acid content, wt. % | Water absorption, wt. % | Tensile strength at break, MPa | Relative elongation at break, % | Time of mold appearance, hours |
|---|---|---|---|---|
| 5 | 370 | 15 | 16 | 214 |
| 10 | 360 | 17 | 19 | > 900 |
| 15 | 350 | 19 | 21 | > 900 |

**Table 7.** Performance properties of hybrid biodegradable biodegradable filled composites based on polylactide, coffee grounds and humic acids

| Polylactide content, wt. % | Content of coffee grounds waste, wt. % | Humic acid content, wt. % | Impact toughness kJ/m$^2$ | Fracture stress in bending, MPa | MFI, g/10 min. | Heating temperature, °C |
|---|---|---|---|---|---|---|
| 60 | 40 | 0.5 | 42 | 420 | 3.3 | 182 |
| 50 | 50 | | 45 | 530 | 3.1 | 186 |
| 40 | 60 | | 27 | 480 | 3.0 | 190 |

Thus, based on the research on the valorization of lignite use, "green" technologies of hybrid polymeric materials modified with humic acids of lignite were created in the form of gelatin hydrogels, biodegradable films of polyvinyl alcohol and hydroxypropyl methyl cellulose and polylactide composites with specified performance properties, suitable for the production of antibacterial gels, patches, masks for human skin, durable waterproof films with antibacterial properties for dry and wet food products with extended shelf life, food containers and packaging, highly selective membranes and microelectronics parts.

## 3. Valorization of Lignite Use in "Green" Technologies

One of the most promising methods of using Ukrainian lignite may be the production of water-soluble sorbents (humic acid salts) for the sorption of heavy metal ions.

Heavy metal ions are very dangerous toxic substances that have a cumulative effect on aquatic life. Insufficiently treated wastewater enters natural water bodies, where heavy metal ions accumulate in water and bottom sediments, thus becoming a source of secondary pollution. They are not removed from the water by mechanical means, nor are they removed by biological treatment and traditional water treatment methods such as coagulation and flotation. This necessitates strict control over their discharge into the environment, which requires the use of relatively inexpensive, accessible means of capturing them. In addition, the current focus of environmental measures on sharply reducing the discharge of untreated wastewater into water bodies requires intensive efforts to develop schemes for the reuse and recycling of treated wastewater and to improve the technology of its deep treatment. The problem of industrial wastewater treatment is becoming increasingly important every year.

The results of the use of humic acids derived from lignite as a sorbent are reported in many scientific publications. Paper [20] presents the results of applying humic acid nanoparticles derived from lignite to inert sand by simple impregnation to obtain a permeable reactive barrier for the purification of groundwater contaminated with copper and cadmium ions. Laboratory studies have shown that the sorption efficiency of such sand is 98% (sorption time - 1 hour; sorbent content 0.25 g/50 mL; pH-7; stirring speed 200 rpm). The results proved that physical sorption was the predominant mechanism of interaction of metal ions and sand with humic acids. The maximum sorption capacity of copper and cadmium was 87.5 and 18.9 mg/L, respectively. Paper [21] shows that the use of a commercially available sorbent based on humic acid bound to silica (HA) allows the removal of aflotoxins from edible oils (tea, canola, peanuts, sunflower, corn, olive, rice, soybeans, sesame). In the literature,[22] the use of iron-based humic acid-coated magnetic nanoparticles (HA-MNPs) for the removal of 2-[4-(dimethylamino)styryl]-1-methylpyridine iodide (2-ASP), as a modular compound for cationic styrylpyridine dyes from aqueous medium, was investigated. Using fluorescence, HA-MNPs were shown to be effective in removing 2-ASP with a maximum adsorption capacity of ~8 mg/L. Kinetic behavior and equilibrium studies have shown that the adsorption process follows the pseudo-2nd order and Langmuir isotherm models. The adsorption is relatively fast, with 70% adsorption completed within 30 minutes, and the total removal is increased by increasing the pH of the solution. Regeneration of HA-MNPs showed that the removal efficiency remained consistently high after five consecutive cycles. The authors of [23] studied the sorption of Cs and Ba on bentonite from the island of Kimolos (Cyclades, Greece) in aqueous solutions in the presence of $Na^+$, $Ca^{2+}$, and humic acid. The experiments were performed using 137Cs and 133Ba as indicators and γ-spectroscopy. It was found that the sorption significantly depends on the initial concentration, ionic strength, and temperature of the solutions, and the sorption isotherms satisfactorily reproduced the Langmuir and Freundlich equations. It was shown that Kimolos bentonite is a good sorbent for Cs and Ba from heavily contaminated solutions, and its sorption capacity decreases in the presence of humic acid and competing cations. The authors of [24] showed that surface-functionalized magnetite nanoparticles treated with humic acid are a promising sorbent for removing U (VI) from industrial waste streams and contaminated waters, but the effect of dissolved inorganic carbon on the mechanism and efficiency of adsorption has not been studied satisfactorily. It was found that the adsorption of U (VI) on $Fe_3O_4$ nanoparticles coated with humic acid does not depend on the ionic strength but increases with decreasing pH and adsorbent concentration. The degree of U (VI) adsorption decreases sharply with increasing concentration of added $NaHCO_3$ and $CaCl_2$ at pH above 5 and 6, respectively.

Work [25] proved that the content of humic acids in solutions of local wastewater inhibits the sorption of metal ions such as Cd, Cr, Cu, Ni, Pb, Zn when using solid commonly used sorbents (BFS, CCF, WTCR, BC). This is due to the formation of stable complexes of humic acids with metal ions, which prevents their sorption by sorbents. The particle size of humates varies in a wide range from 10 to 1000 nm.[26] Given the above, the authors consider the development of a method for water purification by retaining complexes of humic substances with heavy metal ions with ultrafiltration membranes to be a promising direction.

The aim of the study is to develop a method for the use of humic acid salts obtained from the lignite of Ukraine for the sorption of heavy metal ions and their extraction using ultrafiltration membranes.

We studied samples of Ukrainian lignite from the Oleksandriya geological and industrial district. Indicators of technical ($W^a$, $A^d$, $S^d_t$, $V^d$) and elemental ($C^{daf}$, $H^{daf}$, $N^{daf}$, $S^d_t$, $O^{daf}_d$) analyzing lignite, as well as the yield of humic acids $(HA)^{daf}_f$ from it are shown in Table 7.

Analyzing the quality indicators of lignite, it is necessary to note the increased yield of humic acids (79.44%), which will contribute to the economic feasibility of their use for the sorption of heavy metal ions.

Prepared model solutions of metal ions ($Cu^{2+}$, $Pb^{2+}$, $Cd^{2+}$, $Hg^{2+}$, $Zn^{2+}$, $Co^{2+}$) with a concentration of 5 mg/L in distilled water and added complexing agent - humates (sodium salts of humic acids) with different concentrations from 0.0 to 20 mg/dm$^3$.

When purifying solutions from copper ($Cu^{2+}$), lead ($Pb^{2+}$), mercury ($Hg^{2+}$), cadmium ($Cd^{2+}$), zinc ($Zn^{2+}$), and cobalt ($Co^{2+}$) ions, UF-20-PAN membranes (Belarus) were used as ultrafiltration membranes. These membranes are porous polymeric films based on polyacrylonitrile with a pore size of 20 μm, the area of the membrane working surface is $28.26 \cdot 10^{-4}$ m$^2$. Polymeric membranes are characterized by increased heat and aggressive resistance, non-toxic, safe in operation and can be operated at pH from 2 to 12 and a maximum water temperature of 100 $^o$C. The minimum distilled water capacity is 60 dm$^3$/m$^2$·h.

**Table 7.** Lignite quality indicators

| $W^a$ | $A^d$ | $V^d$ | $C^{daf}$ | $H^{daf}$ | $N^{daf}$ | $S^d_t$ | $O^{daf}_d$ | $(HA)^{daf}_f$ |
|---|---|---|---|---|---|---|---|---|
| 16.8 | 48.7 | 29.1 | 61.13 | 5.56 | 0.51 | 3.64 | 29.16 | 79.44 |

The study was carried out in an experimental setup (Fig. 5), which is a non-flow cell with a volume of 0.2 $dm^3$ at an ambient temperature of 25 °C. The solution for separation was poured through a fitting into a transparent cylindrical cell body made of polycarbonate. To reduce the effect of concentration polarization, the cell was equipped with an electromagnetic stirrer and a propeller 3-5 mm away from the membrane. The required pressure (0.2 MPa) above the membrane was created by passing a certain portion of compressed air from the compressor through a valve through special tubes through the fitting. During the separation process, the filtrate that passed through the membrane and drainage through the hole on the lower flange was collected in a sampler and analyzed.

The degree of separation (selectivity, R) of the membrane for the corresponding metal was calculated by the formula:

$$R = \frac{C_0 - C_f}{C_0} \cdot 100 , \quad (1)$$

where *R* – metal ion recovery factor (selectivity), %; $C_0$ and $C_f$ – concentration of metal ions in the initial solution and in the filtrate, respectively, mg/L.

The IR-absorption spectra were recorded on a spectrometer «Nicolet 380» of «Thermo Electron Corporation» firm (USA). Analysis parameters: resolution - 4; recording speed - 0.6329, gain - 4, number of scans – 32. The coal samples under study, humic substances obtained from coal, both before and after interaction with metal ions, were pre-dried and ground. All spectra were recorded in the range of 4000-400 $cm^{-1}$. The interpretation of the IR spectra was based on our own experience as well as on the works of well-known researchers.

For example, in,[27] petroleum ester, carbon disulfide, methanol, acetone, and acetone/sulfur dioxide were chosen as solvents for the ultrasonic extraction of acid-washed lignite from the Hefeng deposit. The extract and the residue were identified as Ei and Ri (i=1, 2, 3, 4, 5) for each stage. Using FT-IR characterization of Ei and Ri, the molecular structure of the extracted product was analyzed by segmented peak fitting. The results show that the hydroxy hydrogen bond in the fifth-order extract is dominated by the self-associated hydroxy hydrogen bond; in the aliphatic substances, only $E_3$ was dominated by the aliphatic $-CH_3$ and asymmetric $-CH_2$ valence vibration, and in the other extracts, the symmetric and asymmetric -CH2 valence vibration was dominated.

$E_1$ is dominated by symmetrical bending vibrations of the $-CH_3$ aliphatic chain end and asymmetrical strain vibrations of $-CH_3$ and $-CH_2$, indicating that petroleum ester mainly breaks the easily breakable chemical bonds in the charcoal samples; $CS_2$ dissolves a larger proportion of the aromatic structure containing aliphatic side chains. The functional groups contained in the five residues are the same, indicating that the basic structure of the coal sample does not change as a result of stepwise extraction. Extraction has an obvious effect on the aromatic structure and hydroxy hydrogen bonding in the residue. The aromatic structures change from a dominant bisubstituted benzene to a dominant tetrasubstituted benzene. Before extraction, the hydroxyl hydrogen bond in the acid-washed char was dominated by hydroxy-ester hydrogen bonds, and after extraction, it was transformed into self-associated hydroxyl hydrogen bonds. In addition, sequential extraction has little effect on oxygen-containing functional groups and aliphatic functional groups. By comparing the structural parameters, it was found that $E_1$, $E_3$ and $R_5$ have a higher degree of aromatic condensation, and $E_4$ has a longer straight and less branched chain.

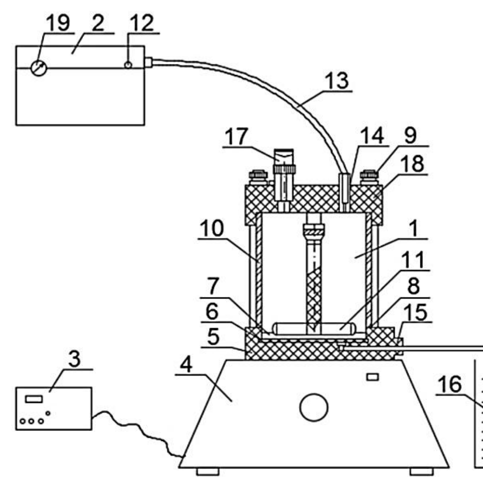



**Fig. 5.** Schematic of the filtration plant: 1 - membrane cell; 2 - compressor; 3 - strobotometer; 4 - magnetic stirrer; 5 - lower base of the cell; 6 - porous fluoroplastic; 7 - membrane; 8 - silicone rubber; 9 - bolts; 10 - cell body; 11 - propeller; 12 - valve; 13 - tube; 14 - fitting; 15 - hole; 16 - sample collector; 17 - safety valve; 18 - upper flange; 19 – manometer

In,[28] attempts were made to construct the molecular structures of vitrified samples from four bituminoses of different ranks and to investigate the relationship between the molecular structure and the thermoplastic properties of vitrified using a number of advanced analytical methods in combination with theoretical methods. Plastometry and the Giseler fluidity index showed that the Evirgol vitrinite had a high fluidity ($F_{max}$=17675 ppm), a wide range of plasticity ($\Delta\tau$=105.1 °C), good adhesion properties (G=99.32). Various analytical techniques, such as 13C solid-state nuclear magnetic resonance spectroscopy, Fourier transform infrared spectroscopy, X-ray diffraction analysis, and Raman spectroscopy, provided comprehensive structural information for the creation of molecular models of vitrinite samples with functional density theory. These molecular models showed that the vitrinite of Evirgol had more cyclic aliphatic structures that contribute significantly to the development of fluidity. These cyclic aliphatic structures may be precursors of aromatic rings in the liquid molecules during coking and provide hydrogen that saturates free radicals in the thermoplastic range. Cyclic aliphatic structures can contribute to the formation of the following molecular structures with a suitable molecular size that maintains the mobile phase in the thermoplastic range to develop fluidity.

In,[29] it was found that native alkaline and alkali-earth metals (AAEM) have obvious catalysis in the pyrolysis of low-grade coal. Due to the differences in the degree of dispersion and chemical form, the catalytic effects of AAEM with different states of occurrence may be different. The chemical structure of the coal is the most direct evidence for the catalysis of AAEM. However, the quantitative characterization and evaluation of these structures, especially the asymmetric functional groups, has always been an unsolved problem. In this study, the FT-IR spectra of Zhundong coals containing different forms of intrinsic AAEM were selected, the functional group structures of these samples were semi-quantitatively characterized by a series of original infrared structural parameters, and the volatile products during pyrolysis were detected by TG-FTIR.

A comprehensive analysis of the structures of functional groups, weight loss rate, and concentration of volatile products indicates that water-soluble and ion-exchangeable AAEM in coal prevents the release/decomposition of -COO- and aliphatic C-H groups and promote thermal cracking of aromatic C-H groups. The inhibition of ion-exchange LLSMs in the release/decomposition of Ar-O- groups and dehydrogenation/polycondensation of aromatic clusters in carbon is also confirmed. The infrared structural parameter method proposed in this paper is expected to be a reasonable, efficient, comprehensive, and versatile method for the quantitative characterization of coal and coal functional group structures, and to improve the existing coal quality analysis method system, respectively, creating a new tool for evaluating and relating coal and coal chemical structures.

The pH value was determined using an ionometer "I-160M" (Ukraine).

The concentration of metal ions in aqueous solutions was determined using a high-resolution optical emission spectrometer PlasmaQuant PQ 9000 Elite (Germany) with inductively coupled plasma.

Infrared spectroscopy was used to study samples of lignite from the Oleksandriya deposit and humic substances obtained from it (Fig. 6).

According to the results of IR spectroscopy, the main functional groups of the studied lignite and humic acids are:

1. Aromatic carbonyl and phenol-containing hydrocarbons, which is confirmed by the presence of an intense band of valence vibrations of C=C bonds at ≈1600 $cm^{-1}$; valence bands of C-O bonds in the region 1705-1650 $cm^{-1}$; intense absorption in the region of valence vibrations of -OH groups (≈3300 $cm^{-1}$), -C-O- groups (1200-1100 $cm^{-1}$), as well as valence and strain bands $C_{ap}$-H at ≈3050 $cm^{-1}$ and 900-700 $cm^{-1}$, respectively. The absorption bands at ≈900 cm-1 are responsible for the vibrations of a single isolated hydrogen atom, at ≈830 $cm^{-1}$, ≈800 $cm^{-1}$, ≈770 $cm^{-1}$ – for vibrations of two, three, and four hydrogen atoms in aromatic rings.

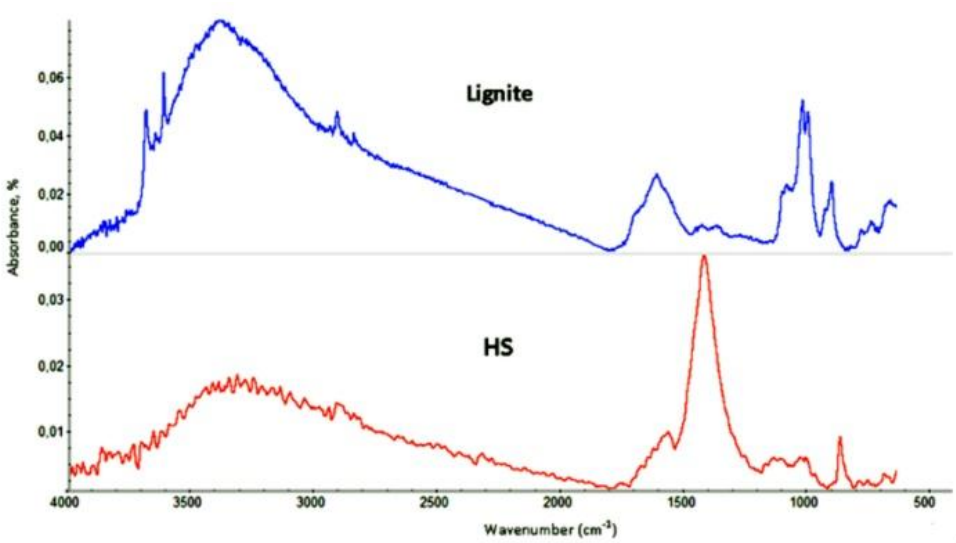



**Fig. 6.** IR spectra of lignite and humic substances

**Table 8**. Concentration of heavy metal ions (mg/L) depending on the concentration of humic substances (mg/L)

| Ion | Concentration of humic substances, mg/L | | | | |
|---|---|---|---|---|---|
| | 0.0 | 2.5 | 5.0 | 10.0 | 20.0 |
| $Cu^{2+}$ | 4.456 | 3.193 | 1.189 | 0.573 | 0.210 |
| $Pb^{2+}$ | 4.259 | 3.449 | 1.071 | 0.541 | 0.257 |
| $Cd^{2+}$ | 4.759 | 3.868 | 2.211 | 1.123 | 0.512 |
| $Hg^{2+}$ | 4.465 | 3.693 | 1.772 | 1.437 | 0.754 |
| $Zn^{2+}$ | 4.422 | 3.823 | 2.088 | 1.477 | 0.542 |
| $Co^{2+}$ | 4.062 | 3.661 | 1.985 | 1.233 | 0.865 |

2. Aliphatic saturated $C_{al}$-H-groups, identified by the presence of absorption bands in the 3000-2800 $cm^{-1}$ ($CH_3$, $CH_2$, CH-groups), as well as asymmetrical stripes (≈1400 $cm^{-1}$) and symmetrical (≈1380 $cm^{-1}$) deformation vibrations of $CH_3$-groups, $CH_2$-groups ≈1485-1445 $cm^{-1}$ and CH-groups - ≈1340 $cm^{-1}$. The bands of C-O-groups (1750-1700 $cm^{-1}$) can be noted - aldehydes, ketones, carboxylic acids, and complex esters.

3. The IR spectra have absorption bands of C-O bonds in simple and complex esters and phenolic C-O groups with a maximum in the region of ≈1280 $cm^{-1}$.

The results of aqueous solution purification from metal ions, depending on the concentration of humic substances (0-20 mg/L), are shown in Table 8 and Fig. 7.Analyzing the graphical dependencies shown in Fig. 7, it can be concluded that with an increase in the concentration of humic substances from 0.0 to 20 mg/L, the selectivity of metal extraction increases, namely: $Cu^{2+}$ from 9.08 to 95.80%; $Pb^{2+}$ from 14.82 to 94.86%; $Cd^{2+}$ from 4.82 to 89.76%; $Hg^{2+}$ from 10.70 to 84.92%; $Zn^{2+}$ from 11.56 to 89.16%; $Co^{2+}$ from 18.76 to 82.70%.

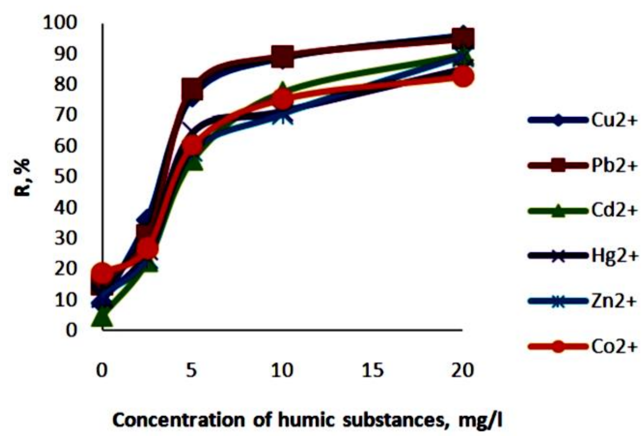



**Fig. 7.** Selectivity of metal ions extraction depending on the concentration of humic substances

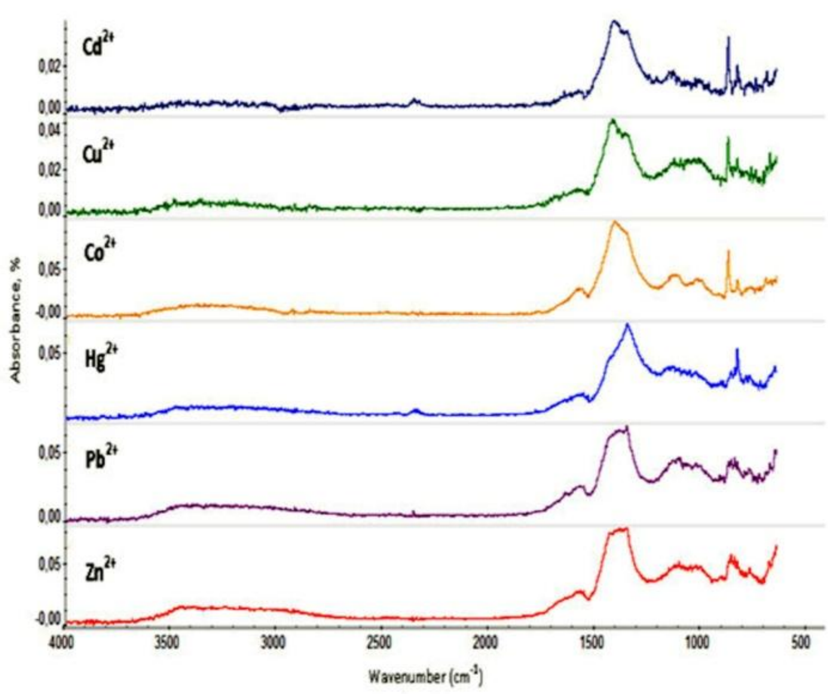



**Fig. 8.** IR spectrum of humic substances after interaction with metal ions

It should be noted that based on the graphical dependencies shown in Fig. 2, the degree of heavy metal ions removal depending on the concentration of humic substances varies nonlinearly. The most optimal concentration of humic substances in terms of metal ion extraction is 5 mg/L, further increase of concentration to 20 mg/L practically does not lead to a significant increase in metal ion extraction.

Fig. 8 shows the IR spectra of humic substances after interaction with heavy metal ions (concentration of humic substances is 5 mg/L).

Thus, based on our research, we can conclude that Ukrainian lignite of the Oleksandriya geological and industrial region contains a large amount (about 80%) of humic acid, which is the basis for the production of effective water-soluble sorbents. It is proved that humic substances isolated from the lignite of Ukraine can bind up to 99% of heavy metal ions in complexes. The most optimal concentration of humic substances in terms of their concentration and selectivity of heavy metal ions removal is 5 mg/L.

## 4. The Application of Lignite Gasification in "Green" Technologies

Lignite gasification is a technological process that involves converting solid fuel into gaseous and liquid products through thermal treatment in the presence of gasification agents, such as oxygen, steam, air, their mixtures, and other chemical reagents.

Currently, a wide range of lignite gasification methods are available, progressing through various stages of research, development, and implementation. In general, lignite gasification can be classified as a "green" technology if it enables the production of syngas with effective removal of acidic components and ensures the environmentally sustainable utilization of liquid by-products—or at least fulfills one of these criteria. This section presents a detailed analysis of the most advanced lignite gasification technologies, along with the potential applications of the products derived from these processes.

Chemical Looping Gasification (CLG) represents an advanced and innovative gasification technology recognized for its potential in the efficient production of synthesis gas. The process operates on the principle of chemical cyclic gasification within a fluidized bed reactor, utilizing phosphogypsum (PG) as an oxygen carrier due to its high calcium sulfate (CaSO□) content.[30] The unique physicochemical properties of the oxygen carrier contribute to enhanced thermal stability and process efficiency, positioning CLG as a competitive alternative to conventional gasification methods. Despite its promise, the technology remains under development and has not yet been deployed at an industrial scale.[31]

The counter-current steam-oxygen gasification of large lignite lumps or briquettes in a fixed bed, commonly referred to as the Lurgi process, has achieved widespread industrial adoption. This process operates by introducing the gasifying agents (steam and oxygen) at the base of the reactor, while the solid fuel is fed from the top, enabling a counter-current movement of gases and solid particles.[32,33] The gasification process is divided into distinct stages: pre-briquetting of lignite, pyrolysis, partial oxidation, and reduction. Due to the inherently high initial moisture content of lignite, which averages 51.2%, effective briquetting requires pre-drying the material to a moisture level of approximately 19%. During the initial stage of the process, moisture is removed in the upper section of the reactor at temperatures ranging from 100 to 200 °C. Further heating to 200–600 °C initiates the thermal decomposition of the organic components of lignite (pyrolysis), accompanied by the release of volatile compounds. The resulting pyrolysis products react with oxygen and steam, leading to the formation of synthesis gas (syngas), whose primary constituents include CO, $H_2$, $CO_2$, $CH_4$, and trace quantities of higher hydrocarbons.[32] The Lurgi process demonstrates several advantages, including high feedstock utilization efficiency and the generation of syngas with a high calorific value. However, it also exhibits certain limitations, particularly the production of substantial quantities of resin compounds and fine particulate matter, necessitating advanced cleaning systems to ensure the quality of the resulting syngas.

Another promising method of lignite gasification is low-temperature gasification, also referred to as oxidative desulfurization of lignite. The essence of this technology lies in converting pyritic sulfur into gaseous sulfur-containing components with minimal oxidant consumption.[34] Research has shown that the sulfur present in lignite, due to its interaction with the organic matrix, is transformed into hydrogen sulfide ($H_2S$). The concentration of gaseous sulfur compounds in the desulfurization gases is significantly higher compared to those in thermal power plant flue gases, enabling their efficient removal using established technologies. The application of oxidative treatment at temperatures of 420–445 °C for durations of 10–21.5 minutes facilitates the conversion of 85–91% of pyritic sulfur into gaseous compounds. This process can significantly reduce sulfur dioxide ($SO_2$) emissions during subsequent coal combustion by 53–77%. Furthermore, the hydrogen sulfide concentration in the desulfurization gases is found to range between 8.0% and 12.5% by volume.[35,36]

Low-temperature oxidative treatment produces the following products:

- Solid fuel with a reduced sulfur content;
- A paste-like mass (resin), formed as a result of the thermal decomposition of the organic components of lignite, with a resin yield of up to 26% by weight, depending on the process conditions;
- Combustible gaseous products (desulfurization gases), which require the removal of hydrogen sulfide ($H_2S$) using established methods.

Given that the low-temperature oxidative treatment of lignite can yield up to 26% resin from the decomposition of the coal's organic matter, this method can also be considered a means of producing liquid products. Since the value of the obtained resin may exceed that of the desulfurized lignite, studies have been conducted to explore potential applications for this resin. Research in [37,38] demonstrated that the addition of CIR coumarone-indene resin (CIR) to bitumen significantly increases its softening point and enhances adhesive properties. However, the addition of CIR also noticeably degrades the plasticity of bitumen, specifically reducing penetration and ductility. To address this issue, it was proposed to use resin derived from the decomposition of lignite organic matter as a plasticizer for polymer-modified bitumen.[39] The results showed that the resin obtained from the low-temperature oxidative treatment of lignite can be effectively utilized as a plasticizer in the production of polymer-modified bitumen. The use of this resin improves the performance characteristics of the bitumen, particularly by enhancing its plasticity without compromising adhesive properties.

The implementation of oxidative technologies effectively reduces the sulfur content in solid fuels and enables the production of high-value secondary products during the gasification process. This contributes significantly to enhancing environmental safety and maximizing the efficiency of lignite resource utilization.

## 5. Conclusions

1. The findings of the conducted study indicate that Ukrainian lignite exhibits substantial potential for utilization within the framework of "green technologies." A comprehensive analysis of the available literature has revealed significant lignite reserves that can be effectively employed in non-energy sectors and environmentally sustainable applications.
2. Experimental results have demonstrated that humic acids extracted from brown coal possess a high degree of functionality and exhibit the capacity for hybrid modification with biodegradable materials, including hydrogels, biofilms, and composite substances. These properties open extensive prospects for the development of innovative, environmentally friendly materials with potential applications in medicine, agriculture, packaging, and other industrial domains.
3. Furthermore, it has been established that humic acids exhibit high efficiency as sorbents for the extraction of heavy metals from industrial wastewater, thereby facilitating ecological remediation and mitigating the adverse environmental impacts of industrial waste.
4. Detailed attention has been devoted to the low-temperature gasification of lignite, a process that enables the production of high-performance additives for polymer-modified bitumen. These additives have significant implications for the advancement of road construction technologies, contributing to the development of more resilient and durable surface coatings.
5. The outcomes of the research underscore the feasibility and relevance of advancing innovative lignite processing technologies under the principles of the European Green Deal. Future research efforts should prioritize the optimization of technological processes for the extraction and utilization of humic acids, as well as the refinement of lignite gasification methodologies, to enhance resource efficiency and ensure ecological sustainability.

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## ВАЛОРИЗАЦІЯ ВИКОРИСТАННЯ ЛІГНІТУ В «ЗЕЛЕНИХ ТЕХНОЛОГІЯХ»

***Анотація.*** *Збільшення використання лігніту в «зелених технологіях» є важливим кроком до раціонального використання і валоризації низькоякісних горючих копалин. У даному дослідженні проаналізовано сучасний стан родовищ бурого вугілля в Україні та розглянуто можливості його застосування в неенергетичних та екологічно «чистих» енергетичних секторах. Досліджено хімічний склад гумінових кислот, отриманих із бурого вугілля, та їхню здатність до гібридної модифікації з біорозкладними матеріалами, такими як гідрогелі, біоплівки та композити. Оцінено потенціал гумінових кислот на основі лігніту як сорбентів для очищення стічних вод від важких металів, що сприяє екологічній ремедіації. Окрему увагу приділено процесу низькотемпературної газифікації лігніту з метою отримання додатків до бітумів, модифікованих полімерами. Отримані результати підтверджують можливість розробки інноваційних методів переробки лігніту відповідно до принципів «зелених технологій».*

***Ключові слова:*** *лігніт, валоризація, "зелені технології", гумінові кислоти, біорозкладні полімери, стійкі матеріали, газифікація лігніту.*