BROWN COAL PROCESSING PRODUCTS UNDER HYDROCAVITATION IMPACT

Denis Miroshnichenko[1], Pavlo P. Karnozhytskyi[1,✉], Oleg Kravchenko[2], Vitalii Homan[2],
Viktoria Taranenkova[1], Pavlo V. Karnozhytskyi[1]

[1] National Technical University – «Kharkiv Polytechnic Institute» (NTU «KhPI»), 2 Kyrpychova St., Kharkiv 61002, Ukraine
[2] Anatolii Pidhornyi Institute of Power Machines and Systems of the NAS of Ukraine, 2/10 Komunalnykiv St., 61046 Kharkiv, Ukraine
✉ *pavlokarnoenv@gmail.com*

Abstract. The study of properties of products of hydrocavitation treatment of lignite from Dnipro lignite coal basin (Dniprobas, Ukraine) has been carried out for the first time. It is shown that as a result of mechanical impact, coal is divided into 3 main components (humic acid solution, residual coal, mineral constituent). The main properties and composition of each component were determined, and microscopic studies of residual coal and mineral particles were carried out. The relevance of the work is determined by the necessity to create a rational waste-free technology of Ukrainian coal processing. The main objective is to find ways to create zero-waste technology for non-thermal processing of brown coal with maximum exploitation of its chemical potential. The method of solving this problem is the use of the hydrocavitation effect on the earthy brown coal of the Mokra Kalyhirka deposit in 1-% aqueous solution of NaOH with subsequent separation of the resulting products. The use of hydrocavitation activation (HCA) provides maximum (up to 95% of the content in the organic mass of coal) extraction of humus acids, obtaining residual coal with sorption properties, and separation of part of the mineral constituent in the form of fine powder with a particle size from 4.3 to 150 microns and chemically corresponding to quartz sand. The practical value of this work is the deep separation of humic acids in the form of sodium salts, as well as obtaining low-cost coal sorbent and finely dispersed mineral constituents suitable for direct use in the manufacture of building materials.
Keywords: brown coal, hydrocavitation activation, humates, sorbent, mineral constituent.

1. Introduction

Brown coal (BC), also known as lignite, is one of the most common mineral resources in the world. Brown coal is a solid combustible mineral that is an intermediate form between peat and hard coal.[1] It contains 58 to 78% carbon[2,3] and has a high moisture content (which can reach up to 60%), while its average calorific value ranges from 9300 to 19300 kJ/kg.[4,5]

The main reserves of brown coal in Ukraine are concentrated in the Dnipro brown coal basin (Dniprobass)[6], which stretches mainly across Right-bank Ukraine within the Zhytomyr, Cherkasy, Kyiv, Zaporizhzhia, Kirovohrad, and Dnipropetrovsk regions. Of the total 2.4 billion tonnes of proven reserves, nearly 0.7 billion tonnes have been developed or prepared for development. Indicated resources and other reserves, totaling approximately 2.5 billion tonnes, are under exploration and represent potential for expanding coal production.[7-9]

According to data from the State Scientific and Production Enterprise "Geoinform of Ukraine" the average ash content of BC in the Dnipro basin ranges from 10.1% to 27.2%; moisture content can reach up to 60.7%, with an average of 56-58%; the volatile-matter yield ranges from 43.7% to 61.7%; total sulfur content varies from 1.28% to 4.99%; the high heat value is between 27.13 and 30.56 MJ/kg; and the low heat value ranges from 7.37 to 9.0 MJ/kg.

At least 50% of Ukrainian brown coal can be extracted using the most efficient method – open-pit mining, which has an energy conversion efficiency 2.5 times higher than underground mining.[10] However, the vast reserves of brown coal in Ukraine are not being developed due to its low quality, in particular high ash content and moisture.[11] At the same time, local coal serves as a source of valuable chemical raw materials.[10-15]

It's worth noting that, due to changes in Ukraine's energy policy, following the EU Directive 2019/944 on common rules for the internal electricity market, specifically regarding the reduction of coal use and extraction in European Union countries, including limitations on CO_2 emissions and other measures to support the transition to a more sustainable energy system, and with

new laws being implemented and the decreasing economic viability of its use,[16] there is currently a significant need to find alternative processing methods and non-traditional uses for coal.

The growing prospects of using lignite as a chemical raw material stimulate the search for methods to enhance its processing efficiency. The greatest interest lies in the possibility of intensifying the processes for obtaining humic and fulvic acids or their salts, the use of which in agriculture is highly promising.[17-20]

Currently, the interest shown in various countries towards the extraction and use of humic acids from coals and peat cannot help but stimulate intensified research in this area with Ukrainian BC. The substantial reserves of this resource in the Dnieper lignite basin offer a powerful potential source of humic acids (HA), whose agricultural application could significantly boost the productivity of the Ukrainian chernozems.

Humic substances (HS) are the main organic component of soils and sediments, widely distributed on the Earth's surface and present in virtually all terrestrial and aquatic environments.[21,22] They play a crucial role as primary carbon accumulators in the biosphere.[23]

The main sources of humic substances include:
- organic matter in soils (60-90%);[23,24]
- peat (40-45%, with up to 60% for woody peat);[25]
- municipal sewage (118-228 mg/g);[26]
- organic matter from lignite (up to 90%);[27]
- and others.

Humic acids, which are soluble in alkaline solutions and insoluble in acidic environments, represent the dominant fraction of HS.[28] They are found in:
- groundwater (20 μg/L) and surface waters (30 mg/L);[29]
- lignites (30-80%);[28]
- peat (10-35%);[28]
- municipal effluents (42% of total HS);[26]
- biomass processing waste (2-10%).[28]

Thus, brown coal is one of the richest sources of humic substances, with colossal global reserves ($\approx$ 4.9 trillion tons to a depth of 600 m).[30] However, it is known that earthy brown coal, which constitutes the majority of the Dnieper brown coal basin, is poorly suited for use as fuel due to its low calorific value and tendency to self-ignite during transportation and storage. The humic acids obtained (with a content of up to 80% in the organic matter of Dnieper basin coal)[31] and humic-containing products from brown coal represent a promising alternative for their use. They fall within the area of deep processing of hydrocarbons, aimed at the comprehensive utilization of coal and increasing the added value of coal products. This is a key component of the Concept of the State Program for the Transformation of Coal Regions in Ukraine.

It should be noted that the analysis of the literature indicates that non-thermal processing of brown coal is primarily focused on the extraction of humic acids, which have recently seen a significantly broader range of applications. At the same time, the solid residues remaining after extraction are either used unqualified or find no application at all. Addressing this issue is the main task of this study.

As mentioned earlier, Ukraine possesses significant reserves of brown coal. A relative characteristic of its geological conditions is its shallow depth, ranging from 5-6 to 100 m in various locations. This creates favorable conditions for open-pit mining, the most cost-effective and safe method.[10,32] Despite these advantageous opportunities, coal extraction has virtually ceased since the early 2000s in several fields of the Dnieper basin.[7] The primary reason for this is the high moisture and ash content of the coal, which significantly diminishes its value as an energy fuel. At the same time, the organic portion of this coal contains an increased amount (up to 80%) of humic acids, which are valuable products used in various sectors of economic activity and environmental protection.[9,12,34,35]

The extraction of humic acids using the traditional scheme is carried out with weak solutions of NaOH or KOH,[36-39] resulting in the formation of water-soluble salts (humates). The process of converting the humic acids of brown coal into a water-soluble form using weak alkaline solutions of sodium or potassium is quite simple; however, it proceeds slowly, requires heating, and does not ensure the complete extraction of the humic component from coals, leading to significant losses of this product.

The intensification of the heterophase process of humate extraction can be achieved through the use of ultrasonic dispersion,[39] ball mills[40] (including with catalytic treatment),[41] microwave treatment,[39] planetary mills,[42] and other methods.

A promising approach, already represented by commercial installations (*e.g.*, UT90-1000, UT37-500), is the use of hydrocavitation treatment, or hydrocavitation activation, or simply hydrocavitation, for the pretreatment of brown coal to intensify the extraction of humic substances processes.

While there is a certain amount of research on HCA as a pretreatment method, specifically for biomass,[43] landfill leachates,[44] municipal wastewater,[45] and hard coal,[46] or as a complete standalone technology,[47] research on the hydrocavitation treatment of brown coal is practically non-existent today.

Previous studies[48,49] demonstrated virtually complete extraction of humic acids (up to 95% of their content), while establishing that the molecular structure of

humic substances remains unchanged under the influence of hydrocavitation. Mineral components are partially separated in pure form during sedimentation, significantly improving the quality of the extracted products and allowing the use of the extracted mineral particles in other industries. Furthermore, the residual coal, after washing to remove humates until the water is colorless, exhibits pronounced sorption properties.[50]

The main objective of this research is to verify the feasibility of creating a waste-free or low-waste technology using hydrocavitation installations and to study the properties of the HCA products of Dnieper Basin brown coal formed during processing.

The use of modern methods of influencing brown coal allows not only for the maximum extraction of humic acids but also creates the possibility of obtaining other valuable products, developing a virtually waste-free technology for the BC processing.

2. Experimental

2.1. Materials

The research object was brown coal sampled from the Mokra Kalyhirka deposit (Cherkasy oblast, Ukraine). The deposit's location is shown in Fig. 1 (the deposit itself is indicated by an orange flag). The composition and main properties of the raw coal are presented in Tables 1-2. The primary reagent was an aqueous NaOH solution manufactured by Supelco, Inc.
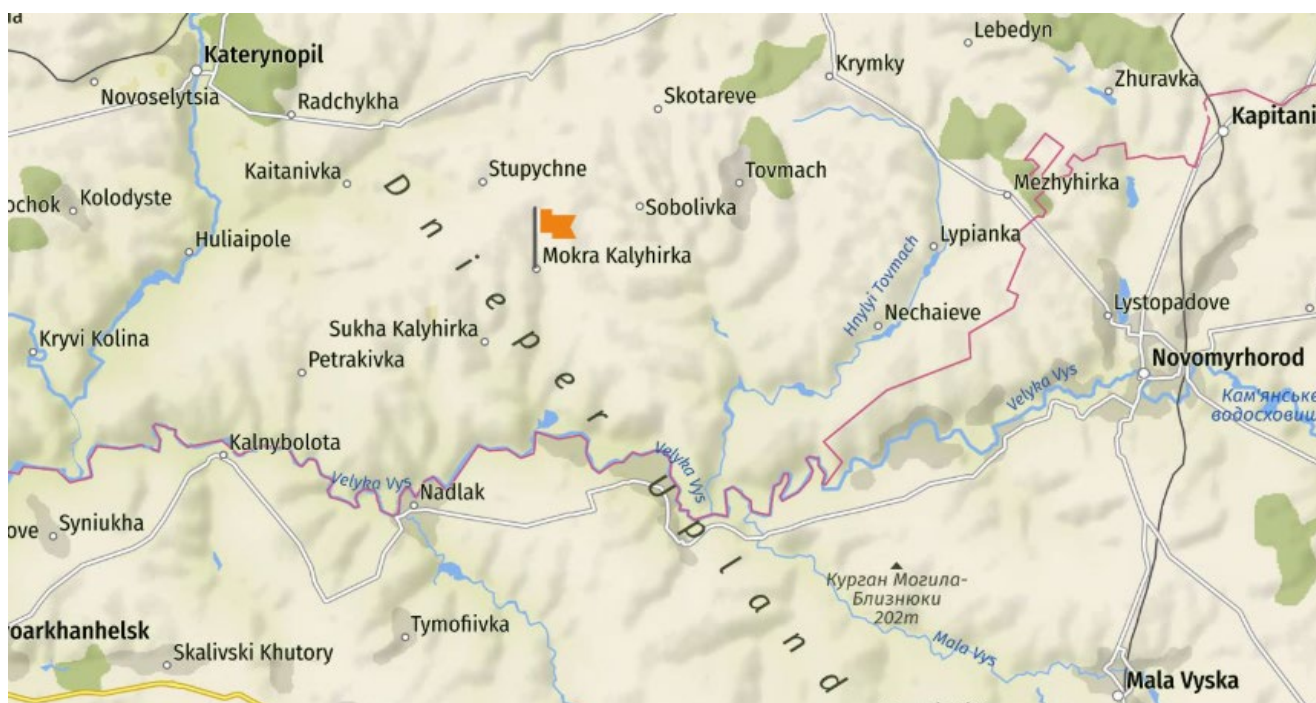

Fig. 1. Mokra Kalyhirka deposit on map

Table 1. Properties of the studied brown coal

Object	Yield, %	A^d	S^d_t	V^d	FC^d, %
Brown coal	100.0	43.4	2.54	33.3	23.3

Table 2. Elemental composition of the research product (dry basis)

Object	C^d	H^d	N^d	S^d_t	O^d_d	Heat of combustion, MJ/kg
Brown coal	39.42	3.49	0.32	2.54	10.82	13.60

2.2. Methods

Standard methods were used for analyzing the coal's composition and properties: ISO 589:2021 (Hard coal — Determination of total moisture), ISO 1171:2010 (Solid mineral fuels — Determination of ash), ISO 562:2010 (Hard coal and coke — Determination of volatile matter), ISO 334:2013 (Solid mineral fuels — Determination of total sulfur — Eschka method), ISO 17246:2010 (Coal — Proximate analysis), ISO 609:2021 (Solid mineral fuels — Determination of carbon and hydrogen — High-temperature combustion method), ISO 333:2020 (Solid mineral fuels — Determination of nitrogen — Semi-micro

Kjeldahl method), and DSTU ISO 1928:2006 (Solid mineral fuels. Determination of gross calorific value by the bomb calorimetric method, and calculation of net calorific value).

The methodology of hydrocavitation activation was used to intensify the physicochemical processes of humic acid extraction from processed brown coal. The coal raw material, previously crushed to a dispersion of 500 microns, based on previous experiments,[48-50] was mixed with a 1% aqueous solution of NaOH in a mass ratio of the components of 1:10, and further preliminary emulsification was carried out using standard mixing equipment (mixers). The resulting mixture was processed by the hydrocavitation activation methodology using technological equipment, the schematic diagram and description of operation of which are given in paper.[48] The cavitation time was 20 minutes. In the course of the process, the mixture temperature increased from 18 to 38 °C, and the pH of the humate solution was ≈10.

During hydrocavitation activation, the coal component is additionally crushed in an aqueous environment by the mechanical impact of the working elements of the technological equipment. Cavitation activation also occurs due to the occurrence of cavitation processes in the treated medium and the subsequent collapse of cavitation bubbles (cavities), during which the coal particles break down into separate organic and mineral components, but with a significantly increased active surface area. These processes actively mix and react the solid phase with the alkaline solution and greatly enhance the process of humic acid extraction. A block diagram of the research process is shown in Fig. 2.
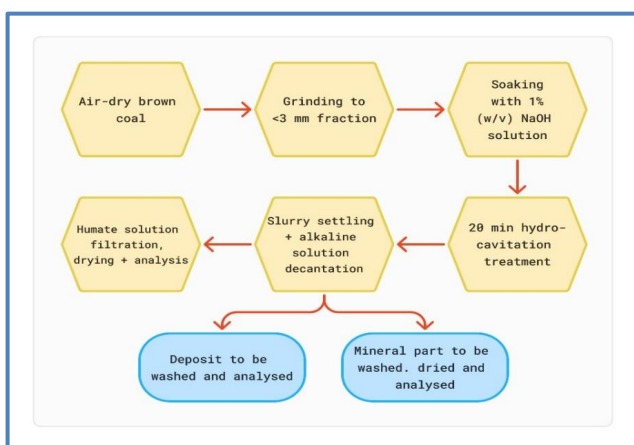

Fig. 2. Block diagram of the research process

The fixed carbon content is calculated as follows:[53]
$$Fixed\ Carbon\ (\%) = 100 - (Moisture\ (\%) - Ash\ (\%) - Volatile\ Matter\ (\%)) \quad (1)$$

Chemical composition analysis of the sand was performed using an Analytik Jena PlasmaQuant PQ 9000 Elite optical emission spectrometer with a Dual View PLUS dual plasma viewing system (Germany). The high-resolution double Echelle monochromator in the instrument allowed for the registration of the analyte line with a resolution of up to 2 pm and its spectral surroundings in 3D mode.

Microscopic studies of the isolated mineral particles were also conducted using a Bresser Erudit MO 20-1536x optical microscope with a Bresser PC-microscope eyepiece (Germany), allowing for image acquisition with a resolution of 640 x 480 pixels, and a Barlow lens enabling maximum image magnification up to 1536x.

3. Results and Discussion

Based on preliminary experiments, a ratio of 1% NaOH solution to coal of 10:1 was selected. The cavitation time was 20 minutes. During this process, the mixture temperature increased from 18 to 38 °C, and the pH of the humate solution was approximately 10.

Hydrocavitation treatment of the BC yielded three main products:
- Alkaline humate solution;
- Residual coal;
- Mineral constituent.

The main properties and elemental composition of the research products are presented in Tables 3-4. The composition of the mineral part is provided in Table 5.

Table 3. Main properties of the research products

Object	Yield, %	A^d	S^d_t	V^d	FC^d, %
Residual coal	22.5	39.6	2.55	42.4	18.0
Dry humates	57.5	26.4	3.72	42.4	31.2
Mineral constituent	20.0	96.4	0.51	3.5	0.1

Table 4. Elemental composition of research products (dry weight basis)

Object	C^d	H^d	N^d	S^d_t	O^d_d	Low heat value, MJ/kg
Residual coal	43.08	4.24	0.06	2.55	10.43	10.66
Dry humates	49.04	4.79	0.42	3.72	15.59	-
Mineral constituent	2.74	0.22	0.00	0.51	0.11	-

Table 5. Composition of the mineral constituents

Indicator	%, mass
K in conversion to K_2O	0.46
Na in conversion to Na_2O	0.3
Al in conversion to Al_2O_3	2.61
Ti in conversion to TiO_2	0.39
Ca in conversion to CaO	0.56
Mg in conversion to MgO	0.19
Fe in conversion to FeO	2.32
P in conversion to P_2O_5	0.015
Si in conversion to SiO_2	84.9
Loss on heating to 450 ºC	6.8
Other	1.455

The composition of the products formed after the cavitation treatment of brown coal indicates a mechanical separation of the raw material into its constituent parts. Analysis of the elemental composition of the obtained products allows us to draw some conclusions about the processes occurring during cavitation. Thus, humates isolated as a 7% aqueous solution (pH = 10.5) after drying have an increased oxygen content (15.59%) compared to the initial coal. This indicates the dissolution of the most oxidized, and therefore the most active, part of the coal. This redistribution of oxygen determines the active properties of humic acids, which are capable of being assimilated by plants and actively bind heavy metal ions in a mobile form.

The carbon content in the products shows the following relationship: the maximum amount of C^d is in the humates (49.04%), an intermediate value is in the residual coal (43.08%), and the minimum value is in the initial coal (39.4%). The amount of hydrogen for all products changes similarly to carbon: for humates – 4.79%, residual coal – 4.24%, initial coal – 3.49%.

Considering that the cavitation treatment results in the separation of an almost pure mineral part (Ad = 96.4%), a decrease in the ash content (39.64%) of the residual coal compared to the initial coal (43.41%) is observed. This determines the increased volatile matter yield for residual coal and humates compared to the initial coal.

The study also included petrographic studies of the mineral part of the coals separated during HCA treatment. The brown coal used in the research is characterized by high ash content, which is generally typical for coals of the entire Dnieper brown coal basin and significantly reduces the value of coal as an energy fuel. Mineral inclusions form intergrowths with the organic part of the coal, which significantly hinders the separation into mineral and organic substances.

As a result of the HCA treatment, the intergrown pieces are destroyed, and a partial separation of the organic mass of coal occurs in the form of a finely dispersed powder and larger, due to greater strength, mineral particles. This creates the prerequisites for a significant reduction in the ash content of the processed coal and facilitates the enrichment process using traditional separation methods, such as flotation or the use of hydrocyclones. During coal processing in the used cavitation apparatus, a partial separation of mineral particles occurs without the use of special enrichment methods.

The chemical composition of the coal's mineral part is given in Table 5. The research results are presented in Figs. 3-5.

Macrodescription

The loose rock, gray in color, contains separate inclusions of dark, almost black color, and is homogeneous (Fig. 3). Based on the size of the fragments, it can be classified as medium-grained clastic (psammite – sands).

Fig. 3. Image of the rock

Microdescription

Under microscopic examination with a single Nicol prism, isometric black inclusions are observed in the sand, likely organic residues. There are also large, irregularly shaped transparent grains among the comparatively smaller ones.

At higher magnification, colorless transparent quartz grains with angular and irregular shapes are noticeable. The larger individual quartz grains have sharp-edged forms and are sometimes covered with a thin brownish film, indicating the presence of limonite (brown iron ore), which is confirmed by the presence of Fe_2O_3 in the sand according to chemical analysis results.

The quartz sand consists of angular, less frequently sharp-edged, quartz grains. It contains impurities of organic matter. The quartz grains contain minute inclusions, and

dark-colored rims around the grains consist of iron oxides; extinction is wavy.

Feldspar impurities ($K[AlSi_3O_8]$ – $Na[AlSi_3O_8]$ – $Ca[Al_2Si_2O_8]$) are present, as indicated by the presence of potassium, sodium, calcium, and aluminum oxides in the sand.

The size of the quartz grains varies widely from 0.15 mm to 0.0043 mm, with the majority ranging from 0.04 mm to 0.02 mm, *i.e.*, the predominant part is less than 0.05 mm. The proportion of large grains ranging from 0.1 mm to 0.15 mm is small.
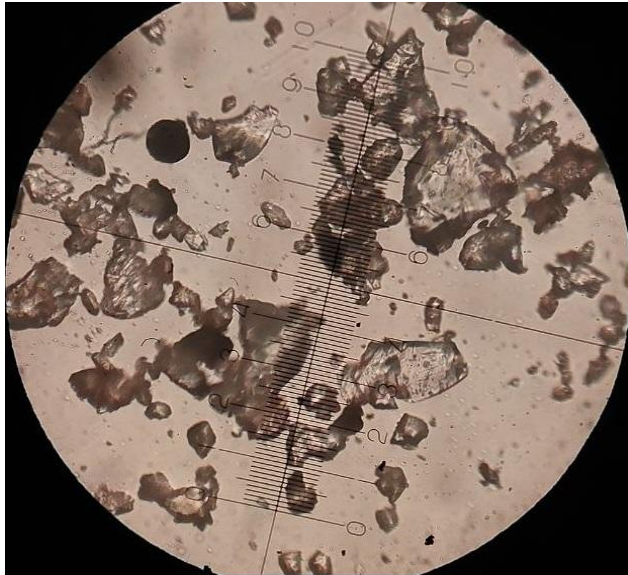

Fig. 4. 240x magnification (1 nicol)

Fig. 5. 240x magnification (1 nicol): predominant fraction – the predominant size – fits the description of fine-grained sands

According to grain size classification, the sand can be categorized as a medium-grained loose rock, specifically as fine-grained (and even very fine) sand with particle sizes less than 0.1 mm (Figs. 4-5). Such particle size allows it to be recommended not as an *aggregate* but as a *filler* for various construction products (*e.g.*, paving slabs, composites, certain autoclave materials), as the grain size corresponds to that of Portland cement powder. Based on its composition, it can be classified as monomineralic, since quartz is its main constituent.

Mechanochemical activation methods are used in the processing of brown coals and lignites to increase the yield of humic and fulvic acids. These acids are colloidal in nature and form on the coal surface depending on the oxidation conditions. As mentioned above, various methods can be employed for this purpose. Mechanochemical treatment of coal significantly increases the yield of humic acids by substantially increasing the surface area of contact between the coal and the alkaline solution during extraction.

Paper[39] notes a 6.3% increase in humic acid yield and a 1% increase in fulvic acid yield due to microwave treatment for 180 seconds. Microwave treatment is noted as being more effective than ultrasonic treatment and conventional mixing with an alkaline solution. Microwave treatment reduces extraction time by a factor of four. Similar effects are observed using a planetary mill[42]. Both studies report an average particle size of 22 nm after processing. However, it is noted that agglomeration may lead to an increase in particle size to an average of 35 nm. The optimal processing time is 20 minutes, resulting in a 14.3% increase in humic acid yield.

It should be noted that in all studies, the main goal of mechanochemical activation is to increase the yield of humic and fulvic acids, which are the most valuable components of brown coals and lignites. However, there is a lack of information regarding the qualified use of the solid residues after extraction – the residual coal and mineral components. Undoubtedly, these components, under the influence of special processing methods, acquire new qualities and can find qualified applications. Therefore, the use of mechanochemical treatment, in particular HCA, on low-metamorphosed oxidized solid fossil fuels can enable the creation of a waste-free technology for processing such raw materials with the production of valuable products.

4. Conclusions

1. The use of HCA on coal from the Dnieper brown coal basin provides virtually complete extraction of humates from the coal structure due to a significant increase in extraction efficiency resulting from increased

surface contact between the crushed coal particles and the alkaline solution.

2. During cavitation treatment, a significant decrease in the ash content of the residual coal after humic substance extraction is observed due to the destruction of coal and mineral matter aggregates and their separation in the turbulent pulp flow.

3. The residual coal, after washing away the water-soluble humates, exhibits properties that allow its use as an effective sorbent.

4. The particle size of the studied sand allows its recommendation as a filler for various building products instead of ordinary quartz sand because the grain size corresponds to the size of Portland cement powder.

5. Comparison of elemental analysis data for the initial coal, residual coal, and humates shows an increase in carbon content for humic acids to 49.04% and a decrease to 43.08% for the residual coal. Humates contain more than 15% oxygen, significantly higher than this parameter for the initial coal.

References

[1] Radzivill, A.Ya. *Bure vuhillia*. Encyclopedia of Modern Ukraine [Online], 2004. https://esu.com.ua/article-38047 (accessed 2024-12-20).

[2] Starzycka, A.; Kasiński, J.; Saternus, A., Urbański, P. *Węgiel brunatny/lignite;* Wydanie II, zaktualizowane; Państwowy Instytut Geologiczny - Państwowy Instytut Badawczy: Warszawa, Poland, 2020.

[3] Marshak, S. *Earth: Portrait of a Planet,* 3rd ed.; W.W. Norton & Company, 2008.

[4] Cox, A.W. Solid fuels. In *Information Sources in Energy Technology*; Butterworth-Heinemann, 1988; pp 173−199.

[5] Grammelis, P.; Margaritis, N.; Karampinis, E. Solid fuel types for energy generation: Coal and fossil carbon-derivative solid fuels. In *Fuel Flexible Energy Generation: Solid, Liquid and Gaseous Fuels,* 1st Edition; Woodhead Publishing, 2016; pp 29−58. https://doi.org/10.1016/B978-1-78242-378-2.00002-X

[6] Pyshyev, S.; Gunka, V.; Bratychak, M.; Grytsenko, Y. Kinetic Regularities of High-Sulphuric Brown Coal Oxidative Desulphurization. *Chem. Chem. Technol.* **2011**, *5*, 107–113. https://doi.org/10.23939/chcht05.01.107

[7] Natsionalnyi hirnychyi universytet, Intekhproekt Ltd. *Potencialnaya rol burogo uglya v energeticheskom balanse strany*. DTEK, 2018. https://dtek.com/content/files/boris-sobko.pdf (accessed 2024-11-06).

[8] Miroshnichenko, D.V.; Pyshyev, S.V.; Lebedev, V.V.; Bilets, D.Yu. Deposits and quality indicators of brown coal in Ukraine. *Naukovyi Visnyk Natsionalnoho Hirnychoho Universytetu* **2022**, *3*, 5–10. https://doi.org/10.33271/nvngu/2022-3/005

[9] Diuzhev, V.; Sinitsyna, A.; Karnozhytskyi, P.P.; Karnozhytskyi, P.V. Sotsialno-ekonomichni, ekolohichni problemy zbilshennia standartiv zhyttiediialnosti naselennia iz zastosuvanniam innovatsiinykh tekhnolohii ochyshchennia

vodnykh resursiv na osnovi vodorozchynnykh sorbentiv otrymanykh z ukrainskoho buroho vuhillia. *Visnyk Natsionalnoho tekhnichnoho universytetu "Kharkivskyi politekhnichnyi instytut" (ekonomichni nauky)* **2022**, *4*, 88–92. https://doi.org/10.20998/2519-4461.2022.4.88

[10] Kulish, V.A. Dobycha burogo uglya v Dneprovskom basseine. *Ugol Ukrainy* [Online] **2015**, *6*, 17–22. http://nbuv.gov.ua/UJRN/ugukr_2015_6_5 (accessed Dec 18, 2024).

[11] Lebedev, V.; Miroshnichenko, D.; Vytrykush, N.; Pyshyev, S.; Masikevych, A.; Filenko, O.; Tsereniuk, O.; Lysenko, L. Novel Biodegradable Polymers Modified by Humic Acids. *Mater. Chem. Phys.* **2024**, *313*, 128778. https://doi.org/10.1016/j.matchemphys.2023.128778

[12] Sinitsyna, A.; Karnozhitskiy, P.; Miroshnichenko, D.; Bilets, D. The Use of Brown Coal in Ukraine to Obtain Water-Soluble Sorbents. *Naukovyi Visnyk Natsionalnoho Hirnychoho Universytetu* **2022**, *4*, 5–10 https://doi.org/10.33271/nvngu/2022-4/005

[13] Pyshyev, S.; Miroshnichenko, D.; Chipko, T.; Donchenko, M.; Bogoyavlenska, O.; Lysenko, L.; Miroshnychenko, M.; Prysiazhnyi, Y. Use of Lignite Processing Products as Additives to Road Petroleum Bitumen. *ChemEngineering* **2024**, *8*, 27. https://doi.org/10.3390/chemengineering8020027

[14] Shustov, O.; Bielov, O.P.; Perkova, T.I.; Adamchuk, A. Substantiation of the Ways to Use Lignite Concerning the Integrated Development of Lignite Deposits of Ukraine. *Naukovyi Visnyk Natsionalnoho Hirnychoho Universytetu* **2018**, *3*, 5–13. https://doi.org/10.29202/nvngu/2018-3/6

[15] The European Parliament, the Council of the European Union. *Directive (EU) 2019/944 on common rules for the internal market for electricity and amending Directive 2012/27/EU (recast)*. Official Journal of the European Union, 2019. https://eur-lex.europa.eu/legal-content/EN/TXT/PDF (accessed 2024-12-25).

[16] Prysiazhny, Y.; Pyshyev, S.; Shved, M.; Pochapska, I.; Niavkevych, M. Plasticizing Additive to Road Bitumens Based on High-Sulfur Brown Coal. *Chem. Chem. Technol.* **2024**, *18*, 623–629. https://doi.org/10.23939/chcht18.04.623

[17] Pleten, V.V. Humaty – novyi metod u rehuliuvanni produktyvnosti. *Naukovi zapysky. Kropyvnytskyi: TsNTU* **2018**, *23*, 164–168.

[18] Gong, G.; Xu, L.; Zhang, Y.; Liu, W.; Wang, M.; Zhao, Y.; Yuan, X.; Li, Y. Extraction of Fulvic Acid from Lignite and Characterization of Its Functional Groups. *ACS Omega* **2020**, *5*, 27953–27961. https://doi.org/10.1021/acsomega.0c03388

[19] Gong, Q.; Wang, L.; Tang, K.; Han, Sh.; Wu, G.; Hu, Z. Preparing Potassium Fulvic Acid Based on Lignite from Different Regions of China. *J. Phys.: Conf. Ser.* [Online] **2022**, *2393*, 012009. https://iopscience.iop.org/article/10.1088/1742-6596/2393/1/012009 (accessed Dec 30, 2024).

[20] Karnozhytskyi, P.P. Perspektyvy neenehretychnoho vykorystannia buroho vuhillia Dniprovskoho baseinu, Suchasni tekhnolohii pererobky palnykh kopalyn: tezy dop. 7-yi Mizhnar. nauk.-tekhn. konf., NTU "KhPI", Kharkiv, Ukraine, April 17-18, 2024.

[21] Tipping, E. *Cation Binding by Humic Substances*; Cambridge University Press, 2005.

[22] Aiken, G.R.; McKnight, D.M.; Wershaw, R.L.; MacCarthy, P. *Humic Substances in Soil, Sediment, and Water: Geochemistry, Isolation, and Characterization*; A Wiley-Interscience Publication, 1985.

[23] Mahler, C.F.; Svierzoski, N.D.S.; Bernardino, C.A. Chemical Characteristics of Humic Substances in Nature. In *Humic Substances*; IntechOpen, 2021; pp 139−153. https://doi.org/10.1093/acprof:oso/9780198738671.003.0004

[24] Trevisan S.; Francioso O.; Quaggiotti S.; Nardi S. Humic Substances Biological Activity at the Plant-Soil Interface: From Environmental Aspects to Molecular Factors. *Plant Signaling Behav.* 2010, *5*, 635–643. https://doi.org/10.4161/psb.5.6.11211

[25] Zhao, H.; Zhou, F.; Bao, X.; Zhou, S.; Wei, Zh.; Long, W.; Yi, Zh. A Review on the Humic Substances in Pelletizing Binders: Preparation, Interaction Mechanism, and Process Characteristics. *ISIJ International* 2023, *63*, 205–215. https://doi.org/10.2355/isijinternational.ISIJINT-2022-306

[26] Alomar, T.; Qiblawey, H.; Almomani, F; Al-Raoush, R.I.; Han, D.S.; Ahmad, N.M. Recent Advances on Humic Acid Removal from Wastewater Using Adsorption Process. *J. Water Process Eng.* 2023, *53*, 103679. https://doi.org/10.1016/j.jwpe.2023.103679

[27] Akimbekov, N.S.; Digel, I.; Tastambek, K.T.; Sherelkhan, D.K.; Jussupova, D.B.; Altynbay, N.P. Low-Rank Coal as a Source of Humic Substances for Soil Amendment and Fertility Management. *Agriculture* [Online] 2021, *11*, 1261. https://www.mdpi.com/2077-0472/11/12/1261 (accessed Dec 28, 2024).

[28] Sarlaki, E.; Paghaleh, A.S.; Kianmehr, M.H.; Vakilian, K.A. Valorization of Lignite Wastes into Humic Acids: Process Optimization, Energy Efficiency and Structural Features Analysis. *Renew. Energy* 2020, *163*, 105–122. https://doi.org/10.1016/j.renene.2020.08.096

[29] Wang, M.; Liao, L.; Zhang, X.; Li, Zh. Adsorption of Low Concentration Humic Acid from Water by Palygorskite. *Appl. Clay Sci.* 2012, *67-68*, 164–168. https://doi.org/10.1016/j.clay.2011.09.012

[30] Lysenko, L.A.; Miroshnychenko, D.V.; Bohoiavlenska, O.V. *Huminovi rechovyny: otrymannya, vykorystannya*, Suchasni tekhnolohii pererobky palnykh kopalyn: tezy dop. 6-yi Mizhnar. nauk.-tekhn. konf., NTU "KhPI", Kharkiv, Ukraine, April 11-12, 2023.

[31] Karnozhytskyi, P.P. *Zabrudnennia gruntovoho pokryvu ta yoho vidnovlennia za shliakhom sumisnoho zastosuvannia HK ta zakhodiv z fito rekultyvatsii*, Suchasni tekhnolohii pererobky palnykh kopalyn: tezy dop. 6-yi Mizhnar. nauk.-tekhn. konf., NTU "KhPI", Kharkiv, Ukraine, April 11-12, 2023.

[32] Sinitsyna, A.O.; Karnozhytskyi P.P. Bure vuhillia – syrovyna dlia otrymannia vodorozchynnykh sorbentiv. *Intehrovani tekhnolohii ta enerhozberezhennia* 2023, *3*, 67–77. https://doi.org/10.20998/2078-5364.2023.3.06

[33] Sinitsyna, A. O.; Karnozhytskyi, P.V. *Oleksandriiske bure vuhillia yak dzherelo huminovykh rechovyn*, Suchasni tekhnolohii pererobky palnykh kopalyn: tezy dop. 5-yi Mizhnar. nauk.-tekhn. konf., NTU "KhPI", Kharkiv, Ukraine, April 14-15, 2022.

[34] Zhylina, M.; Karnozhytskyi, P.P.; Miroshnichenko, D.; Konohrai, V.; Sterna, V.; Ozolins, J. The Effect of Growth Stimulants Based on Humic Acids from Ukrainian Lignite and Biochar from Agricultural Residues on the Growth and Development of Lettuce (*Lactuca sativa*). *Agron. Res.* [Online early access] 2025, *23*, 571–584. https://doi.org/10.15159/ar.25.013 (accessed Apr 15, 2025).

[35] Symanowicz, B.; Toczko, R. Brown Coal Waste in Agriculture and Environmental Protection: A Review. *Sustainability* 2022, *15*, 13371. https://doi.org/10.3390/su151813371

[36] Haider, R.; Ghauri, M.A.; Akhtar, K. Isolation of Coal Degrading Fungus from Drilled Core Coal Sample and Effect of Prior Fungal Pretreatment on Chemical Attributes of Extracted Humic Acid. *Geomicrobiol. J.* 2021, *32*, 944–953. https://doi.org/10.1080/01490451.2015.1039673

[37] Fatima, N.; Jamal, A.; Huang, Z.; Liaquat, R.; Ahmad, B.; Haider, R.; Ali, M.I.; Shoukat, T.; Alothman, Z.A.; Ouladsmane, M. *et al.* Extraction and Chemical Characterization of Humic Acid from Nitric Acid Treated Lignite and Bituminous Coal Samples. *Sustainability* [Online] 2021, *13*, 8969. https://doi.org/10.3390/su13168969 (accessed Jan 20, 2025).

[38] Cheng, G.; Niu, Z.; Zhang, C.; Zhang, X.; Li, X. Extraction of Humic Acid from Lignite by KOH-Hydrothermal Method. *Appl. Sci.* 2019, *9*, 1356. https://doi.org/10.3390/app9071356

[39] Aftab, K.; Javed, J.; Siddiqua, U.H.; Malik, A.; Hassan, A.; Khan, M.R.; Busquets, R.; Ahmad, N.; Haque, A. Process Optimization and Method Validation for Efficient Valorization of Low- Grade Coal into Humic Substances. *Fuel* 2024, *369*, 131796. https://doi.org/10.1016/j.fuel.2024.131796

[40] Tang, Y.; Yang, Y.; Hou, S.; Cheng, D.; Yao, Y.; Zhang, S.; Xie, J.; Wang, X.; Ma, X.; Yu, Z.; Li, S. Multifunctional Iron–Humic Acid Fertilizer from Ball Milling Double-Shelled Fe–N-doped Hollow Mesoporous Carbon Microspheres with Lignite. *ACS Sustain. Chem. Eng.* 2021, *9*, 717–731. https://doi.org/10.1021/acssuschemeng.0c06406

[41] Sun, Q.; Xu, C.; Geng, Z.; She, D. Extraction and Characterization of Humic Acid with High Bio-Activity by Mechanical Catalytic Treatment. *Ind. Crops Prod.* [Online] 2023, *206*, 117623. https://www.sciencedirect.com/science/article/abs/pii/S092666902 3013882 (accessed Jan 2, 2025).

[42] Skybová, M.; Turčániová, Ľ.; Čuvanová, S.; Zubrik, A.; Hredzák, S.; Hudymáčová, Ľ. Mechanochemical Activation of Humic Acids in the Brown Coal. *J. Alloys Compd.* 2007, *434-435*, 842–845. https://doi.org/10.1016/j.jallcom.2006.08.310

[43] Desikan, R.; Thangavelu, K.; Uthandi, S. Hydrodynamic Cavitation – A Promising Technology for Biomass Pretreatment. *J. Environ. Sci. Nat. Resour.* [Online] 2019, *19*, 556015 https://juniperpublishers.com/ijesnr/IJESNR.MS.ID.556015.php (accessed Jan 10, 2025).

[44] Bis, M.; Montusiewicz, A.; Ozonek, J., Pasieczna-Patkowska, S. Application of Hydrodynamic Cavitation to Improve the Biodegradability of Mature Landfill Leachate. *Ultrason. Sonochem.* 2015, *26*, 378–387. https://doi.org/10.1016/j.ultsonch.2015.03.003

[45] Lebiocka, M. Application of Hydrodynamic Cavitation to Improve the Biodegradability of Municipal Wastewater. *J. Ecol. Eng.* [Online] 2020, *21*, 155–160.

https://doi.org/10.12911/22998993/123163 (accessed Jan 29, 2025).

[46] Han, H.; Liu, A.; Wang, H. Effect of Hydrodynamic Cavitation Assistance on Different Stages of Coal Flotation. *Minerals* [Online] **2020**, *10,* 221. https://www.mdpi.com/2075-163X/10/3/221 (accessed Dec 31, 2024).

[47] Nedbailo, A.; Ivanytsky, G.; Tselen, B.Y.; Radchenko, N.; Gozhenko, L.; Shchepkin, V. Application of a Pulsating Dispersor as a Hydrodynamic Cavitation Reactor for Preparation of Coal Water Fuel. *Thermophysics and Thermal Power Engineering* [Online] **2023**, *45*, 28–34. https://doi.org/10.31472/ttpe.1.2023.4 (accessed Dec 6, 2018).

[48] Kravchenko, O.; Miroshnychenko, D.; Karnozhytskyi, P.P; Homan, V.; Karnozhytskyi, P.V. Intensifying the Process of Extraction of Humic Acids from Brown Coal by Using the Hydrocavitation Activation Methodology. *Int. J. Energy Clean Environ*. **2025**, *26*, 61–75. https://doi.org/10.1615/InterJEnerCleanEnv.2024053521

[49] Karnozhytskyi, P.P.; Karnozhytskyi, P.V.; Zhylina, M. Rozrobka malovidkhodnoi tekhnolohii pererobky buroho vuhillia, Suchasni tekhnolohii pererobky palnykh kopalyn: tezy dop. 7-yi Mizhnar. nauk.-tekhn. konf., NTU "KhPI", Kharkiv, Ukraine, April 17-18, 2024.

[50] Melnikov, A.; Miroshnychenko, D.; Karnozhytskyi, P.P.; Karnozhytskyi, P.V. Sorption Properties of Brown Coal Processing Products*. Chem. Chem. Technol.* **2024**, *18*, 493–501. https://doi.org/10.23939/chcht18.04.493

[51] Kravchenko, O.; Suvorova, I.; Baranov, I.; Goman, V. Hydrocavitational Activation in the Technologies of Production and Combustion of Composite Fuels. *East.-Eur. J. Enterp. Technol.* **2017**, *4*(5(88)), 33–42. https://doi.org/10.15587/1729-4061.2017.108805

[52] Suvorova, I.; Kravchenko, O.; Goman, V.; Baranov, I. Criteria for Assessing the Energy-Ecological Effectiveness of using the Sludge of Waste Treatment Plants as Components of Liquid Composite Fuels. *Eur. J. Sustain. Dev.* **2020**, *9*, 328–336. https://doi.org/10.14207/ejsd.2020.v9n4p328

[53] Anshariah, H.; Imran, A.M.; Widodo, S.; Irfan, U.R. Correlation of Fixed Carbon Content and Calorific Value of South Sulawesi Coal, Indonesia. *IOP Conf. Ser.: Earth Environ. Sci.* **2020**, *473*, 012106. https://doi.org/10.1088/1755-1315/473/1/012106

ПРОДУКТИ ПЕРЕРОБКИ БУРОГО ВУГІЛЛЯ В УМОВАХ ГІДРОКАВІТАЦІЙНОГО ВПЛИВУ

Анотація. Уперше проведено дослідження властивостей продуктів гідрокавітаційної обробки бурого вугілля Дніпровського буровугільного басейну (Україна). Показано, що в результаті механічного впливу вугілля розділяється на 3 основні компоненти (розчин гумінових кислот, залишкове вугілля, мінеральна складова). Визначено основні властивості та склад кожного компонента, проведено мікроскопічні дослідження залишкового вугілля та мінеральних частинок. Актуальність роботи визначається необхідністю створення раціональної безвідходної технології переробки українських вугіль. Основною метою є пошук шляхів створення безвідходної технології нетермічної переробки бурого вугілля з максимальним використанням його хімічного потенціалу. Методу вирішення цієї проблеми є використання гідрокавітаційного впливу на землисте буре вугілля в 1-% водному розчині NaOH з подальшим розділенням утворених продуктів. За використання гідрокавітаційної активації (НСА) забезпечується максимальне (до 95% від вмісту в органічній масі вугілля) вилучення гумусових кислот, отримання залишкового вугілля, що має сорбційні властивості, та виділення частини мінеральної складової у вигляді дрібнодисперсного порошку крупністю від 4.3 до 150 мкм і відповідного за хімічним складом кварцевому піску. Практичною цінністю цієї роботи є глибоке виділення гумусових кислот у формі натрієвих солей, а також отримання дешевих вугільних сорбентів і дрібнодисперсної мінеральної складової, придатної для безпосереднього використання у виробництві будівельних матеріалів.

Ключові слова: буре вугілля, гідрокавітаційна активація, гумати, сорбент, мінеральна складова.