

OPTIMISATION OF THE EXTRACTION PROCESS OF TOLUENE
AND HUMIC ACID EXTRACT FROM BROWN COAL

Denis Miroshnichenko^{1,2,*}, Maryna Zhylina^{3,4,5}, Oleksandr Bielov¹, Liudmyla Lysenko¹,
Mykhailo Miroshnychenko¹, Hennadii Omelianchuk¹, Serhiy Pyshyev⁶, Jurij Ozolins³

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Abstract. Lignite (brown coal) is a promising source of humic acids (HAs) and toluene-soluble extracts (bitumen "A"), which have applications as soil conditioners/biostimulants (HAs) and hydrophobic coatings or polymer additives (toluene extract). This study optimized their sequential extraction from Ukrainian lignite, evaluating yield trade-offs and structural properties. Four extraction variants were tested. Conventional toluene-first extraction (Variant 0) yielded the highest toluene extract (14.86 wt. %), but lower HAs (41.0 wt. %), while reversing the sequence (Variants 2–3) increased HA yields (47.39–51.70 wt. %) at the expense of toluene extract (1.79–5.28 wt. %). Structural analysis revealed toluene extracts had higher aromaticity (60.1–61.9% aromatic carbon) and molecular association (1.9–2.2) than HAs (48.5–60.3%; 1.6–2.0), reflecting their distinct chemistries. Alkaline pretreatment enhanced HA aromaticity but reduced toluene extract recovery. The findings enable tailored protocols for agricultural (HAs) or industrial (toluene extract) applications, supporting sustainable lignite valorization.

Keywords: lignite, humic acids, toluene extract, bitumen A, extraction, optimization.

1. Introduction

Lignite, or brown coal, is a low-grade coal characterized by a high moisture content, high volatile matter, and significant proportions of oxygen-containing functional groups. Although it is primarily used as a fuel, lignite also serves as a promising raw material to produce high-value organic compounds such as humic acids (HAs) and toluene-soluble substances (commonly referred to as bitumen "A" or montan wax). The extraction and utilization of these substances from lignite is gaining increasing attention due to their potential applications in agriculture, environmental technology, materials science, and industry.^{1–3} In recent years, lignite valorization has become a focal point of green chemistry and industrial ecology, aiming to transform low-grade fossil resources into high-value functional products.

Humic substances (HSs), including humic acids, fulvic acids, and humin are the most important components of natural organic matter in soils and sedimentary environments. These compounds are the products of complex biochemical and chemical transformations of plant and microbial residues over time.^{4,5} Humic acids, the alkali-soluble and acid-precipitable fraction of HSs, are particularly significant due to their large molecular size, abundant functional groups (*e.g.*, carboxylic and phenolic), and high reactivity.⁶ These properties make HAs efficient in various environmental and industrial processes, including soil improvement, wastewater treatment, polymer reinforcement, and biostimulant formulations.^{7–9} The chemical complexity of HAs enables unique interactions with metals, nutrients, and organic pollutants, making them effective carriers and stabilizers in environmental and agricultural applications.¹⁰ Toluene-soluble extracts from lignite, on the other hand, primarily consist of lipophilic substances such as esters, alcohols, hydrocarbons, and resinous materials. These are presumed to be derived from preserved plant waxes or represent

¹National Technical University Kharkiv Polytechnic Institute, 2 Kirpychova St., Kharkiv 61000, Ukraine

²State Enterprise "Ukrainian State Research Institute for Carbochemistry (SE "UKHIN), 7 Vesnina St., Kharkiv 61023, Ukraine

³Riga Technical University, Faculty of Natural Sciences and Technology, Institute of Biomaterials and Bioengineering, 3 K-1, Paula Valdena St., Riga LV-1048, Latvia

⁴Institute of Agricultural Resources and Economics, Stende Research Centre, Dizzemes, Dizstende, Libagu parish, Talsu County, LV-3258, Latvia

⁵Institute of Materials and Surface Engineering, Faculty of Natural Sciences and Technology at Riga Technical University, 7. P. Valdena St., Riga LV-1048, Latvia

⁶Lviv Polytechnic National University, 12 S. Bandery St., Lviv 79013, Ukraine

* dvmir79@gmail.com

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secondary products formed during the geochemical transformation of organic matter.¹¹⁻¹³ Montan waxes and similar extracts are used in cosmetics, polishes, lubricants, and composite materials due to their stability and hydrophobic nature.¹⁴ These substances are promising as functional additives in polymer matrices, adhesives, and biodegradable films, suggesting opportunities for material innovation from lignite resources.¹⁵

The increasing global demand for sustainable and value-added products from natural resources has prompted research into improved extraction methods of HAs and toluene extracts from lignite. Traditional techniques, while effective, often fail to account for the complex interactions between extraction steps, reagent concentrations, temperature profiles, and the sequence in which different substances are removed. Furthermore, these processes can significantly influence the structural and compositional integrity of the products, especially for substances with high sensitivity to environmental parameters such as temperature and pH.¹⁶ For instance, uncontrolled extraction may result in partial oxidation or condensation of reactive molecular fragments, reducing solubility and altering the functional group profile of the extracted substances. Standard extraction methods are constantly being modernized to improve their efficiency.¹⁷ Previous studies have investigated acid/oxidative pretreatment (*e.g.*, HNO₃, H₂O₂), biological liquefaction using fungi, and process optimization through advanced reactor design and statistical modeling techniques.¹⁸⁻²¹ These studies demonstrate improved yields and more favorable elemental composition, including higher carbon content and lower ash or moisture. Advanced process designs such as membrane ultrafiltration, ultrasonic-assisted extraction, and microwave-assisted treatment have also shown promising results.²²⁻²⁴ The research gap remains in simultaneously or sequentially optimizing the extraction of both toluene extract and humic acids. There is a lack of comprehensive studies examining how the extraction order affects the yield and molecular properties of the products. For instance, alkaline extraction before toluene extraction may reduce bitumen yield but enhance humic acid recovery, and vice versa. Moreover, the incorporation of toluene-soluble fractions into the HA matrix during alkali treatment suggests an interconversion or chemical bonding potential between these fractions.^{25,26} Some researchers have suggested that aromatic and aliphatic fractions within the organic matrix may undergo partial cross-linking or depolymerization, depending on solvent polarity and extraction kinetics. Our study addresses this gap by analyzing multiple extraction routes and systematically altering the conditions-mass of lignite samples, concentration and volume of reagents, extraction temperature and duration, and apparatus configuration. The

goal is to develop a refined methodology that allows controlled separation and tailored compositional profiles of both HAs and toluene extracts. In doing so, we also investigate the empirical limitations of current analytical formulas used for estimating parameters such as aromatic carbon content and hydrogen unsaturation in lignite samples, particularly of low metamorphic grade. Furthermore, the structural characterization of the resulting products is essential for linking process parameters to product performance. Techniques such as FTIR spectroscopy, elemental analysis, thermogravimetric analysis (TGA), and scanning electron microscopy (SEM) offer insights into the stability, molecular architecture, and surface morphology of extracted materials.²⁷ Understanding these correlations enables the development of predictive models for extraction efficiency and quality optimization.

The scientific and practical significance of this work is underscored by the expanding interest in humic substances such as soil conditioners and biostimulants in sustainable agriculture, especially under the EU's Green Deal and global climate mitigation policies^{28,29} as well as biochar.³⁰ Additionally, valorizing lignite through the recovery of valuable organic components aligns with circular economy strategies, minimizing waste and improving the economic viability of lignite-based industries.³¹ These efforts contribute to reducing reliance on petrochemical feedstocks and enhancing the sustainability of resource management systems. HSs are a good sorbent for the removal of heavy metals from the soil.³²⁻³⁴ Currently, the issue of soil remediation from heavy metals has become particularly pressing due to ongoing military activities in Ukraine, which increases the value of this study.

By addressing the structural behavior of lignite-derived materials under various extraction conditions, this research contributes to both the theoretical understanding of humic substance formation and the practical development of green, resource-efficient technologies. Ultimately, the outcomes of this study will support the scaling-up of optimized processes for the industrial extraction of humic acids and toluene extracts, offering a pathway for lignite to serve as a sustainable source of multifunctional organic materials. The resulting process design can further inform policy and industrial stakeholders regarding best practices for resource-efficient and environmentally responsible coal valorization.

The aim of the study is to develop optimal conditions for obtaining toluene extract and humic acids from Ukrainian brown coal, as well as to determine the indicators of their technical and elemental analyses, aromatic carbon content, degrees of hydrogen unsaturation, and molecular association of the organic matter.

2. Experimental

Fig. 1 is a schematic representation of the research procedure for optimizing the extraction of toluene extract and humic acids (HAs) from Ukrainian brown coal.

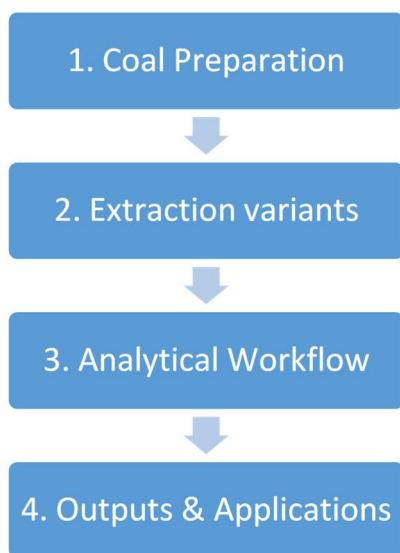


Fig. 1. Schematic representation of the research procedure

The diagram outlines the sequential steps involved in the four experimental variants (0–3), highlighting key stages such as sample preparation, solvent extraction, and analytical processes. Variant 0 involves toluene extraction followed by alkaline treatment for HAs, while Variants 1–3 explore alternative sequences, including alkaline pretreatment before toluene extraction. The schematic also depicts the use of standardized methods (*e.g.*, ISO 975:2021 for toluene extract and ISO 5073:2021 for HAs) and equipment like the extraction apparatus. Figure 1 visually summarizes the workflow, emphasizing the variables tested (*e.g.*, solvent volume, temperature, and extraction duration) and their impact on yield and product properties. This structured approach enables a clear comparison of the extraction protocols and their outcomes, supporting the study's goal of optimizing lignite valorization for industrial or agricultural applications.

2.1. Materials

To determine the quality indicators of coal, the following standard methods were applied: ISO 18283:2022 Coal and coke - Manual sampling; DSTU 4096–2002 Brown coal, bituminous coal, anthracite, oil shale, and coal briquettes. Methods for sampling and sample preparation for laboratory testing; DSTU 8699:2016 (ISO 18283:2022) Hard coal, anthracite, and coke. Manual sampling; ISO 17246:2010 Coal - Proximate analysis; ISO 334:2020 Coal

and coke - Determination of total sulfur; ISO 589:2008 Two methods for determining total moisture content of hard coals, a two-stage method and a single-stage method; ISO 1170:2020 Coal and coke - Calculation of analyses to different bases; ISO 17247:2020 Coal and coke - Ultimate analysis; ISO 975:2021 Brown coals and lignites – Determination of yield of benzene-soluble extract – Semi-automatic method; ISO 5073:2021 Brown coals and lignites – Determination of humic acids.

Table 1 presents the quality indicators of the Ukrainian brown coal sample used in our study.

Table 1. Data of proximate and ultimate analyses of Ukrainian brown coal

Proximate analysis, % (wt.)		Ultimate analysis, % (wt.)				
W ^a	A ^d	C ^d	H ^d	N ^d	S ^d _t	O ^d _d
21.6	20.9	56.1	4.1	0.6	4.9	13.4

According to ISO 11760:2005 the coal is classified as low-rank coal; according to ASTM D388-12 the coal falls under Class Lignite A or Lignite B.

Based on the data presented in Table 1, including total moisture content, ash content, and elemental composition, it can be concluded that the coal belongs to a low stage of metamorphism, industrial grade 1B, or weakly coalified (soft) coal. Visually, this coal is characterized as “earthy brown coal.” In its natural state, the studied brown coal is a moist, loose, low-grade fuel that oxidizes and spontaneously ignites during storage, indicating a high content of heteroatoms: oxygen up to 26% wt., nitrogen up to 1.0% wt., and sulfur up to 5.0% wt.

This Ukrainian brown coal, unlike other grades of brown coal, is characterized by a high oxygen content in various functional groups that bind carbon and hydrogen atoms in its structure. According to current understanding of coal structure, the organic matter (OM) is heterogeneous and includes two or even three phases in its structure, composed of various aromatic and hydroaromatic fragments connected by aliphatic or ether “bridges.” At the same time, various data suggest that aromatic structures dominate the OM, although coal similar to the sample under study also contains a significant number of aliphatic structures.

The diversity of structures and, consequently, coal properties are determined by the quantitative ratio of different types of interactions, functional groups, and structural fragments. Since the studied coal type is weakly coalified (soft), its maximum solubility is expected when interacting with various solvents.

The structural parameters of the toluene extract and humic acids were calculated using known formulas:

1. The value of C_{ar} characterizes the content of aromatic carbon in the organic matter relative to its total carbon content:

$$C_{ar} = 3,4 \cdot \frac{C^{daf}}{100 - C^{daf}} \quad (1)$$

2. The parameter δ , which characterizes the degree of hydrogen unsaturation of a unit mass of organic matter, is calculated by the formula:

$$\delta = \frac{C^{daf}}{6} - H^{daf} + \frac{O^{daf} + N^{daf} + S_t^d}{21}, \quad (2)$$

where C^{daf} , H^{daf} , N^{daf} , O^{daf} and S_t^d are the elemental contents in the organic matter of coal, % wt.

3. The cA parameter, indicating the degree of molecular association of organic matter, is calculated as:

$$cA = 1 - \frac{H^{daf} + 0.125 \cdot (O^{daf} + N^{daf} + S_t^d)}{0.333 \cdot C^{daf}}, \quad (3)$$

where C^{daf} , H^{daf} , N^{daf} , S_t^d are the elemental contents in the coal, % wt.

2.2. Methods

Table 2 presents the conditions for performing the research, namely: the procedure and determination of the yield of toluene extract and free humic acids.

Table 2. Conditions for conducting the study

Stage	Variant			
	0	1	2*	3*
1. Determination of the yield of toluene extract				
1.1 Sample weight, g	17.216	26.736	14.823	10.234
1.2 Volume of toluene, cm ³	150	230		
1.3 Extraction conditions	4 hours in the extraction apparatus	1. Single heating ~100 °C. 2. 6 hours in a drying cabinet at 40-50 °C. 3. 18 hours at 20-22 °C. 4. Single heating >70 °C		4 hours in the extraction apparatus
2. Determination of the yield of free humic acids				
2.1 Sample weight, g	3.646	22.752	26.370	26.227
2.2 Volume of NaOH, cm ³ (% vol.)	100(1)	200(2)		
2.3 Boiling in a water bath, hours	2			
2.4 Washing. Volume of NaOH, cm ³ (% vol.)	2×100(1)	2×165(2)		
2.5 Volume of HCl, cm ³ (% vol.)	60(5)			
3. Determination of the yield of toluene extract from humic acids				
3.1 Sample weight, g	Not determined			13.030
3.2 Volume of toluene, cm ³				230
3.3 Extraction conditions				4 hours in the extraction apparatus

* stage 2 was performed before stage 1

Variation "0". The determination of the toluene extract was carried out according to ISO 975:2021. The essence of the method is as follows. A sample of brown coal is extracted with toluene in an extraction apparatus. Then, the solvent is distilled off, and the dissolved residue is dried to a constant weight. The yield of the toluene extract in percentage is calculated by the mass of the residue after drying, and the result is given for the dry state of the fuel. The determination of the yield of free humic acids was carried out according to ISO 5073:2021 (from bituminized coal). The essence of the method is a single extraction of humic acids from the analytical coal sample after removing the toluene extract with a 1% solution of sodium hydroxide by heating, precipitation of humic acids with an excess of hydrochloric acid, and determining the mass of the residue.

Variation "1". Compared to Variation "0," the sample mass and solvent volume were increased. Instead of the extraction apparatus, the following heating scheme was used: 1. Single heating to ~100 °C; 2. Heating for 6 hours in a drying oven at 40-50 °C; 3. Aging for 18 hours at 20-22 °C; 4. Single heating >70 °C. All coal remaining after determining the yield of the toluene extract was used to determine the yield of free humic acids. Due to the increased mass of the coal sample, the concentration and volume of NaOH for both boiling and washing were nearly doubled.

Variation "2". The determination of the yield of free humic acids was carried out before the determination of the toluene extract. All procedures were identical to those in Variation "1". The determination of the toluene extract was conducted on dehumidified coal (after the removal of humic acids).

Variation "3". The determination of the yield of free humic acids was also performed before determining the toluene extract. The method for determining the yield of humic acids was identical to that used in Variations 1 and 2. The toluene extract was determined using an extraction apparatus, with the volume of toluene reaching 230 cm³,

applied to dehumidified coal. The procedure for determining the toluene extract from the humic acids was the same as in Variation 1, specifically using an extraction apparatus with a toluene volume of 230 cm³.

During the experiments, the yields of the products were calculated, as well as the indicators of their technical and elemental analyses.

The extraction apparatus used for determining the toluene extract is shown in Figure 1. The extraction apparatus Fig.2 consists of the following components: a flat-bottomed conical flask with a 500 cm³ capacity and a 40/30 ground joint; a reflux condenser with a 40/30 ground joint and a minimum length of 400 mm; and an extraction sleeve made of filter paper, 30 mm in diameter and 90 mm in length, placed in a mesh frame.

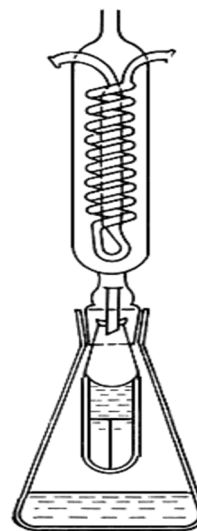


Fig. 2. Apparatus for determining toluene extract

3. Results and Discussion

Table 3 summarizes the yield and quality indicators of toluene extract and humic acids (HAs) extracted from Ukrainian brown coal across four experimental variants (0–3).

Table 3. Yield and quality of the tested samples

Variant	Sample	Yield, % wt	Proximate analysis, % (wt.)		Ultimate analysis, % (wt.)			
			W ^a	W ^a	C ^d	H ^d	N ^d +S ^d +O ^d	
1	2	3	4	5	6	7	8	
0	0.1	Toluene extract	14.86	1.8	0.3	78.6	11.9	9.2
	0.2	Coal after toluene extraction	85.14	9.9	24.5	52.2	2.7	20.6
	0.3	Humic acids, HA ^{daf} _f	41.00	11.2	3.9	57.4	3.8	34.9
	0.4	Coal after treatment with NaOH (1 %)	59.00 ¹	12.3	30.4	46.0	3.3	20.3

Table 3. (Continuation).

	1	2	3	4	5	6	7	8
1	1.1	Toluene extract	5.32	2.0	0.1	79.6	12.4	7.9
	1.2	Coal after toluene extraction	94.68	10.4	22.1	54.8	3.6	19.5
	1.3	Humic acids, HA ^{daf} _f	51.70	17.3	5.3	51.8	4.5	38.4
	1.4	Coal after treatment with NaOH (2 %)	48.30 ²	11.0	46.3	36.1	3.4	14.2
2	2.1	Humic acids, HA ^{daf} _f	48.32	14.2	5.1	61.7	4.0	29.2
	2.2	Coal after treatment with NaOH (2 %)	51.68	11.8	41.3	42.9	4.0	11.8
	2.3	Toluene extract	1.790	1.7	0.3	79.6	12.6	7.5
	2.4	Coal after toluene extraction	98.21 ³	13.5	42.0	45.5	4.2	8.3
3	3.1	Humic acids, HA ^{daf} _f	47.39	14.1	5.0	61.8	4.1	29.1
	3.2	Coal after treatment with NaOH (2 %)	52.61	11.6	41.0	43.0	4.0	12.0
	3.3	Toluene extract	5.28	1.8	0.3	79.9	12.9	6.9
	3.4	Coal after toluene extraction	94.72 ⁴	13.4	42.3	45.7	4.3	7.7
	3.5	Toluene extract from humic acids	0.48	Not determined				

¹ when calculating the yield of samples 0.3 and 0.4, the yield of sample 0.2. is taken as 100%

² when calculating the yield of samples 1.3 and 1.4, the yield of sample 1.2. is taken as 100%

³ when calculating the yield of samples 2.3 and 2.4, the yield of sample 2.2. is taken as 100%

⁴ when calculating the yield of samples 3.3 and 3.4, the yield of sample 3.2. is taken as 100%

Variant 0 yielded the highest toluene extract (14.86 wt. %) but lower HAs (41.00 wt. %), while Variants 1–3 prioritized HA recovery (47.39–51.70 wt. %) at the expense of toluene extract yields (1.79–5.32 wt. %), demonstrating that extraction sequence and conditions significantly influence product distribution. Proximate analysis revealed toluene extracts were pure, with low moisture (1.7–2.0 wt. %) and ash (0.1–0.3 wt. %), whereas HAs contained higher moisture (11.2–17.3 wt. %) and ash (3.9–5.3 wt. %), reflecting their hydrophilic and mineral-rich nature. Ultimate analysis showed toluene extracts were carbon-dense (78.6–79.9 wt. %) with elevated hydrogen (11.9–12.9 wt. %), characteristic of hydrocarbon-rich fractions, while HAs had lower carbon (51.8–61.8 wt. %) and higher heteroatom content (29.1–38.4 wt. %), consistent with their oxygenated functional groups. Residual coal post-extraction exhibited increased ash (up to 46.3 wt. %) and reduced carbon (36.1–52.2 wt. %), confirming the removal of organic components. The data highlight a trade-off: traditional methods (Variant 0) favor toluene-soluble bitumen, while modified protocols (Variants 1–3) enhance HA yields, likely due to alkaline pretreatment disrupting the coal matrix. These findings underscore the tunability of extraction processes to target specific fractions—hydrophobic waxes for industrial applications or oxygen-rich HAs for agricultural use – while also revealing the

structural complexity of lignite, where aliphatic and aromatic domains respond differently to solvent and alkaline treatments. The table thus provides critical insights for optimizing lignite valorization strategies based on desired product profiles.

Figs. 3 and 4 show photographs of toluene extract and humic acids.

**Fig. 3.** Photo of toluene extract**Fig. 4.** Photo of humic acids

Table 4. presents the structural characteristics of toluene extracts and humic acids (HAs) derived from Ukrainian brown coal across four experimental variants (0-

3), focusing on three key parameters: aromatic carbon content, degree of hydrogen unsaturation, and degree of molecular association.

Table 4. Structural Characteristics of Toluene Extracts and Humic Acids from Brown Coal

Variant	Sample Type	Aromatic Carbon Content, %	Degree of Hydrogen Unsaturation	Degree of Molecular Association
0	Toluene Extract	61.9	0.94	2.2
	Humic Acids	55.7	0.64	1.8
1	Toluene Extract	61.4	0.89	2.1
	Humic Acids	48.5	0.55	1.6
2	Toluene Extract	60.1	0.85	1.9
	Humic Acids	60.2	0.74	2.0
3	Toluene Extract	60.8	0.88	2.0
	Humic Acids	60.3	0.73	2.0

The toluene extracts consistently exhibited higher aromatic carbon content (60.1-61.9% wt.) compared to HAs (48.5-60.3% wt.), reflecting their more condensed, hydrocarbon-rich nature, though HA aromaticity increased significantly in Variants 2-3 (60.2-60.3% wt.) when extracted prior to toluene treatment, suggesting alkaline pretreatment may liberate aromatic clusters from the coal matrix. The hydrogen unsaturation values, which indicate electron deficiency in the organic structure, were higher for toluene extracts (0.85-0.94) than HAs (0.55-0.74), aligning with their greater aromaticity and lower heteroatom content. Molecular association, a measure of cross-linking density, followed a similar trend, with toluene extracts showing stronger intermolecular interactions (1.9-2.2) versus HAs (1.6-2.0), consistent with their more hydrophobic and aggregated nature. Notably, Variant 1 HAs displayed the lowest aromaticity (48.5%) and molecular association (1.6), likely due to the aggressive alkaline conditions fragmenting larger aromatic domains, while Variants 2-3, which reversed the extraction sequence, yielded HAs with structural metrics closer to toluene extracts, implying shared molecular features. These structural differences underscore how extraction order and conditions selectively target distinct coal fractions: toluene isolates aromatic, highly associated lipophilic components, while alkaline extraction captures more polar, less condensed HA networks. The data reveal that process optimization can tune molecular architecture, which is critical for applications where aromaticity (*e.g.*, material stability) or solubility (*e.g.*, agricultural bioavailability) are key factors. Table 4 thus bridges process parameters to molecular outcomes, guiding tailored lignite valorization.

Despite using the same lignite source and applying the standardized alkaline extraction protocol, the yields and characteristics of humic acids (HAs) obtained in Variants 1, 2, and 3 varied significantly. These differences can be attributed to the sequence of extraction and the resulting

physicochemical state of the coal matrix at the time of alkaline treatment. In Variant 1, the toluene extract was removed before HA extraction, likely disrupting the hydrophobic domains in the coal matrix. This may have exposed more polar sites for alkaline interaction but also led to partial oxidation or rearrangement of the remaining organic matter, reducing the yield and quality of HAs. Indeed, this variant produced the highest HA yield (51.70 wt. %) but with lower aromatic carbon content (48.5 wt. %) and weaker molecular association (1.6), suggesting that the aggressive conditions fragmented larger aromatic domains and solubilized less structurally integrated humic material. In contrast, Variants 2 and 3 applied alkaline extraction before toluene extraction, allowing HAs to be removed from a more intact organic matrix. This preserved larger aromatic clusters, resulting in lower HA yields (47.39–48.32 wt. %), but with higher aromaticity (60.2–60.3%) and greater molecular association (2.0), indicating structurally denser humic fractions. Moreover, because some lipophilic compounds may have remained bound within the coal matrix during NaOH treatment, they may have co-precipitated with HAs or altered the solubility dynamics. Thus, the variation among these variants highlights that even small differences in the sequence of solvent application can lead to non-linear effects on extraction behavior due to changes in matrix porosity, polarity, and molecular interactions. This reinforces the need to tailor extraction strategies based on the desired end-use: maximum yield vs. structural quality.

The current study optimized the extraction of toluene extract (yields: 1.79-14.86 wt. %) and humic acids (HAs; yields: 41.00-51.70 wt. %) from Ukrainian brown coal, revealing their structural properties (*e.g.*, aromatic carbon content: 48.5-61.9%). In contrast, references³⁵⁻⁴¹ expanded on these findings by applying HAs in advanced materials, such as thermosensitive hydrogels,^{35,39} biodegradable polymers,^{37,38} and road bitumen additives.³³ While the article

focused on extraction efficiency and structural characterization, the referenced works demonstrated practical enhancements: ³⁵ and ³⁷ showed improved mechanical and thermal properties in HA-modified biopolymers, and ³⁶ utilized lignite-derived extracts to enhance petroleum bitumen performance. Additionally, ⁴⁰⁻⁴⁵ explored brown coal for water-soluble sorbents, aligning with the article's emphasis on lignite valorization. The structural metrics (*e.g.*, aromaticity, molecular association) reported in the article provided a foundation for the functional modifications in ³⁵⁻⁴¹, bridging fundamental research with industrial and environmental applications. Together, these studies highlight the versatility of lignite-derived products, from optimized extraction to innovative uses in materials science and engineering.

4. Conclusions

This study aimed to optimize the extraction process of toluene extract and humic acids (HAs) from Ukrainian brown coal, while analyzing their structural and compositional properties. The methodology involved four experimental variants (0-3) that altered extraction sequences and conditions, including solvent volumes, temperatures, and alkaline treatments, followed by proximate/ultimate analyses and structural characterization. The main findings revealed that: (1) Variant 0 yielded the highest toluene extract (14.86% wt.) but lower HAs (41.0% wt.), whereas reversing the extraction order (Variants 2-3) increased HA yields (47.39-51.70% wt.) at the expense of toluene extract (1.79-5.28% wt.); (2) toluene extracts exhibited higher aromatic carbon (60.1-61.9%) and molecular association (1.9-2.2) than HAs (48.5-60.3% and 1.6-2.0, respectively), reflecting their hydrocarbon-rich nature; and (3) alkaline pretreatment enhanced HA aromaticity (up to 60.3%) but reduced toluene extract yields, highlighting trade-offs between product selectivity and efficiency.

However, limitations include the use of a single coal type, which may restrict generalizability, and the lack of kinetic studies to refine extraction durations. Additionally, the environmental impact of solvent use and energy-intensive steps warrants evaluation for industrial scalability. Future work should explore: (1) hybrid extraction techniques (*e.g.*, ultrasound/microwave-assisted methods) to improve yields and reduce processing time; (2) advanced characterization (*e.g.*, NMR, pyrolysis-GC/MS) to elucidate molecular transformations during extraction; and (3) field trials to assess HAs' agronomic efficacy and toluene extracts' performance in material applications. By addressing these gaps, the research can advance toward sustainable, high-value lignite valorization aligned with circular economy goals.

Abbreviations

Abbreviation/Symbol	Definition
HAs	Humic acids
HSs	Humic substances
OM	Organic matter
FTIR	Fourier-transform infrared spectroscopy
TGA	Thermogravimetric analysis
SEM	Scanning electron microscopy
C _{ar}	Aromatic carbon content (%)
δ	Degree of hydrogen unsaturation
cA	Degree of molecular association
W ^a	Total moisture content (%)
A ^d	Ash content (dry basis, %)
C ^{d/daf}	Carbon content (dry basis/dry ash free basis, %)
H ^{d/daf}	Hydrogen content (dry basis/dry ash free basis, %)
N ^{d/daf}	Nitrogen content (dry basis/dry ash free basis, %)
S ^{d_t}	Total sulfur content (dry basis, %)
O ^{d_d}	Oxygen content (dry basis, %)
HA ^{daf_f}	Humic acids (dry ash-free basis)
NaOH	Sodium hydroxide
HCl	Hydrochloric acid
EU	European Union

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ОПТИМІЗАЦІЯ ПРОЦЕСУ ЕКСТРАКЦІЇ ТОЛУОЛЬНОГО ЕКСТРАКТУ ТА ГУМІНОВИХ КИСЛОТ З БУРОГО ВУГІЛЛЯ

Анотація. Лігніт (буре вугілля) є перспективним джерелом гумінових кислот (ГК) і толуолорозчинних екстрактів (бітум "А"), які застосовують як ґрунтові кондиціонери/біостимулятори (ГК) та гідрофобні покриття або полімерні добавки (толуольний екстракт). У цьому дослідженні оптимізовано їхню послідовну екстракцію з українського лігніту, оцінюючи компроміси виходу та структурні властивості. Було протестовано чотири варіанти екстракції. Звичайна екстракція спочатку толуолом (варіант 0) дала найвищий екстракт толуолу (14,86 мас.%), але нижчий вміст ГК (41,0 мас.%), тоді як зворотна послідовність (варіанти 2–3) збільшила вихід ГК (47,39–51,70 мас.%) завдяки екстракту толуолу (1,79–5,28 мас.%). Структурний аналіз показав, що толуольні екстракти мали вищу ароматичність (60,1–61,9% ароматичного вуглецю) та молекулярну асоціацію (1,9–2,2), ніж ГК (48,5–60,3%; 1,6–2,0), що відображає їхній різний хімічний склад. Попередня лужна обробка посилювала ароматичність ГК, але зменшувала вилучення толуольного екстракту. Отримані результати дають змогу розробляти адаптовані протоколи для сільсько-господарського (ГК) або промислового (толуольний екстракт) застосування, що сприяє сталому використанню лігніту.

Ключові слова: лігніт, гумінові кислоти, толуольний екстракт, бітум А, екстракція, оптимізація.