Infrared Spectroscopic Study of the Mechanisms of Humic Acid Precipitation in Aqueous Acid Solutions

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ABSTRACT

This study investigated the mechanisms of Humic Acid (HA) precipitation from brown coal waste using hydrochloric, sulfuric, citric, and ascorbic acids. Precipitation was conducted at a pH range of 1.47 to 2.01, and the resulting HAs were characterized by CHN elemental analysis and Fourier Transform Infrared (FTIR) spectroscopy. The highest HA yield was obtained with ascorbic acid (94.81%), followed by sulfuric (93.08%), hydrochloric (91.03%), and citric acid (89.31%). The elemental analysis revealed that citric and ascorbic acids promoted greater preservation of oxygen-containing functional groups (C: 36.4% and 34.8%, respectively), while mineral acids led to more condensed aromatic structures. FTIR spectra confirmed variations in aromaticity, hydroxyl, carboxyl, and carbonyl group intensities, indicating significant structural differences depending on the acid used. These findings suggested that organic acids can offer a milder alternative for HA recovery, preserving functional groups critical for sorption and complexation. The proposed approach contributes to the valorization of coal waste and supports the development of environmentally friendly materials for use in agriculture, water treatment, and soil remediation.

Keywords-humic acids; precipitation; organic acids; IR spectroscopy; organogenic composition

I. INTRODUCTION

HAs are complex natural organic macromolecules that play a crucial role in soil formation, the migration of metals and organic pollutants, and in water purification technologies. Their behavior in aquatic environments, particularly their precipitation in acidic changes, remains a pressing issue for ecology, chemistry, and material science [1].

Infrared (IR) spectroscopy is one of the most informative techniques for examining the chemical structure and functional groups of HAs, as well as the mechanisms of their precipitation [2, 3]. This method enables the identification of spectra changes associated with protonation, complexation, and aggregation. The vibration analysis of characteristic functional groups, such as carboxyl (–COOH), phenolic (–OH), and carbonyl (C=O), provides insights into the chemical interactions that occur during coagulation and flocculation [4]. In addition, IR spectroscopy contributes to the tracking of conformational shifts in HAs molecules, which is critical for understanding the procedures of their self-assembly and stabilization of colloidal systems. When combined with pH variation, this technique enables the analysis of how acidity influences HA structure and interactions, which is an important aspect in modeling their behavior in natural and technological

processes. Among the first scientists that employed this method were authors in [5], who studied in detail the chemical structure of HAs and their functional groups, developing the basis for a further understanding of their properties and interactions. Later, authors in [6, 7] also contributed to this topic by expanding spectroscopic methods and detailing their structural characteristics, focusing on the influence of various factors, such as pH and the presence of metals, on the behavior and structure of HAs in natural and industrial systems.

The mechanisms of HA precipitation in aqueous solutions have been the subject of active research for many years. Early work in this area has focused on the effect of pH on HA solubility and coagulation [8]. Additionally, authors in [9] found that acidification of solutions to pH equal to 1-2, led to HA precipitation, which was associated with the protonation of carboxyl and phenolic groups, reducing their solubility [9]. Later studies examined the effect of various factors on the precipitation process, including electrolyte concentration, the presence of polyvalent cations and organic compounds. In [10], the addition of salts, such as sodium or calcium chloride, promoted HA coagulation by screening the negative charges on the surface of the molecules, reducing electrostatic repulsion while increasing aggregation. The utilization of the hydrochloric acid (HCl) solution is one of the most widely applied and standardized approaches for the extraction and purification of humic substances from natural sources, including soils, peat, coal, and aquatic systems. This method is based on lowering the pH of the solution to a level at which HAs lose their solubility, coagulate, and precipitate. The key physicochemical processes underlying the precipitation of HAs in the presence of HCl include the protonation of carboxyl and phenolic groups, which decrease their ionization ability, and electrostatic repulsion between humic molecules, leading to aggregation, flocculation, and precipitation at a pH below 2-3, as humates become insoluble. This technique has been thoroughly studied and optimized, leading to its standardization as International Standard ISO 5073-85 [11].

While the precipitation of HAs using mineral acids is well-documented, the impact of organic acids on the structural and chemical properties of precipitated HAs remain poorly understood. Previous studies have focused primarily on optimizing yield and purity, with limited attention being paid to how different acidifying agents induce the functional group composition, aromaticity, and elemental profile of humic substances.

Therefore, this study aims to investigate the precipitation mechanisms of HAs using both mineral (hydrochloric and sulfuric) and organic (citric and ascorbic) acids, with a focus on identifying the resulting differences in structure and functional group preservation.

II. MATERIALS AND METHODS

A. Raw Materials and Reagents

The raw material used in this study consisted of brown coal mining waste collected from spoil heaps near the Shoptykol open-pit mine of the Maikuben deposit (Central Kazakhstan). The coal waste was preliminarily crushed and ground using a laboratory mill to achieve particle fractions that maximize the yield of humic substances.

The procedure for HA extraction involved a sequential treatment of coal samples to isolate and subsequently precipitate humic compounds. The extraction was performed as follows: the coal waste samples were treated with an alkaline solution of sodium pyrophosphate ($Na_4P_2O_7$) to break the bonds between humic substances and the mineral matrix of the coal. The samples were then heated with a sodium hydroxide (NaOH) solution, which facilitated the dissolution of HAs and their transition into the liquid phase.

B. Acidification and Precipitation Method for Humic Acids

The precipitation of HAs from the extract was carried out by acidification of the solution. This process was based on the reduction of the pH of the medium at which the protonation of carboxyl (-COOH) and phenolic (-OH) groups of HAs occurred, decreasing their solubility and resulting in precipitation.

Various mineral and organic acids were used: hydrochloric acid, sulfuric acid, citric acid, and ascorbic acid. The precipitation process started with the gradual addition of acid into the alkaline extract of HAs under continuous stirring until a pH of 1-2 was achieved. The solution remained at room temperature for 12 hours to complete the coagulation process. The resulting precipitate were separated by vacuum filtration and washed several times with portions of distilled water to remove any residual acid and dissolved salts. The washing process was carried out until the onset of HA peptization, which was determined by the appearance of a slight yellow coloration in the filtrate. Figure 1 illustrates the step-by-step precipitation procedure.

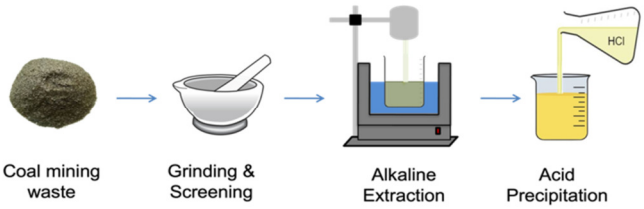

Fig. 1. Scheme of the experiments.

The precipitated HAs were dried at a temperature of 90 ± 5 °C in a drying oven until a constant mass was achieved. For further structural analysis of humic compounds, the precipitates were subjected to ashing at 600 ± 25 °C, which allowed for the removal of the organic component and the study of inorganic impurities in the composition of humic substances.

The yield of HAs was calculated using:

$$(H)_t^{daf} = \frac{(m_1 - m_2)V}{V_1 m} 100\% \quad (1)$$

where: m_1 is the mass of dry HAs in grams, m_2 is the mass of HA ash in grams, V is the total volume of the alkaline solution in the volumetric flask (cm³), V_1 is the volume of the alkaline solution aliquot taken for HA precipitation (cm³), and m is the dry, ash-free, and bitumen-free mass of the sample used to determine the HA yield in grams.

C. Analytical Methods

The study was conducted using a FTIR Spectrometer, IR Prestige-21 (SHIMADZU, Japan), which operates based on the Fourier transform principle. This instrument allows for the simultaneous recording of IR spectra over a wide range (7800 to 350 cm^{-1}), with high spectral resolution up to 0.5 cm^{-1}, enabling a detailed analysis of functional groups, their identification, and identification of the subtle changes in the chemical structure of HAs.

The KBr-pellet method was deployed for IR spectrum acquisition, due to its high transparency in the IR range, which minimizes background absorption and allows for the acquisition of a clear and precise spectrum of HAs. The precipitated HAs were dried until a constant mass was achieved to eliminate the influence of moisture. The dried sample was then finely ground in an agate mortar to obtain a fine powder. A small portion of the sample (1-2 mg) was thoroughly mixed with dry, anhydrous KBr (200-300 mg). The mixture was placed into a pressing matrix and subjected to a pressure of 10,000-15,000 psi to form a transparent KBr pellet. The KBr pellet containing HAs was placed in the optical path of the spectrometer.

Measurements were conducted at room temperature (25 ± 2°C) in a dry atmosphere to avoid the influence of moisture. For each sample, 3 to 5 spectra were recorded, and the data were averaged to improve accuracy. The spectrometer resolution was set to 4 cm^{-1}, with 64 scans performed, ensuring a high level of spectral detail. Processing of IR spectra, quantitative absorption analysis, and spectral database search were carried out using IRsolution software (SHIMADZU). The analysis aimed to identify characteristic absorption bands corresponding to various functional groups of HAs. To assess their structural changes during precipitation with different acids, the relative absorption intensity of carboxyl, phenolic, and carbonyl groups was compared, along with shifts in the region of aromatic bonds.

To determine the elemental composition of HAs, specifically the mass fraction of carbon (C), hydrogen (H), and nitrogen (N), an elemental analysis using a CHN analyzer was performed. This method is based on the complete combustion of the sample in an oxygen atmosphere at high temperatures, followed by the analysis of the resulting gaseous products. Specifically, a dried sample (~2-3 mg) was placed into the reactor of the analyzer. The sample was combusted at 900-1100 °C in a pure oxygen atmosphere, ensuring the complete oxidation of the organic phase. As a result of the reaction: carbon (C) was converted into carbon monoxide (CO), hydrogen (H) was transformed into water vapor (H_2O), and nitrogen (N) into nitrogen oxides (NO_x). The NO_x generated during combustion were reduced to molecular nitrogen (N_2) before entering the detector. Carbon monoxide (CO) was oxidized to carbon dioxide (CO_2) in an oxidation chamber. Water vapor (H_2O) was either removed or analyzed using appropriate detectors.

III. RESULTS AND DISCUSSION

The organogenic composition is a key characteristic of HAs, as it reflects their chemical nature, degree of aromaticity, oxidation state, and potential interaction mechanisms with metal ions and other compounds.

The results of the elemental composition analysis of HAs precipitated using different acid agents are presented in Table I.

TABLE I. ORGANOGENIC COMPOSITION OF THE OBTAINED HAs

Acid type	pH	Organogenic element (%)					HA yield (%)
		C	H	N	O	S	
Hydrochloric acid	1.47	31.5	4.7	2.8	11.15	1.6	91.03
Sulfuric acid	1.52	33.2	4.4	2.3	12.65	1.8	93.08
Citric acid	1.86	36.4	5.8	2.1	13.78	1.2	89.31
Ascorbic acid	2.01	34.8	5.2	2.5	12.09	1.3	94.81

It was observed that the organogenic composition of precipitated HAs depended on the type of acid used. The highest carbon content was recorded in samples precipitated with citric acid (36.4%) and ascorbic acid (34.8%), indicating a greater preservation of the organic framework and a high degree of aromaticity in these compounds. In contrast, sulfuric and hydrochloric acid precipitation resulted in lower carbon content (33.2% and 31.5%, respectively), which may suggest partial oxidation and degradation of aromatic structures in more aggressive acidic environments. The hydrogen content also varied, reaching its maximum with citric acid precipitation (5.8%), demonstrating a higher proportion of aliphatic compounds or a lower degree of condensation of humic substances. Sulfuric and hydrochloric acids, on the other hand, contained less hydrogen (4.4-4.7%), confirming their possible aromatization and degradation of saturated hydrocarbon fragments. Nitrogen was mainly present in amine groups and heterocyclic compounds [12], with its content ranging from 2.1% (citric acid) to 2.8% (hydrochloric acid). The high nitrogen concentration in HAs precipitated with hydrochloric acid may be due to better stabilization of nitrogen-containing functional groups, whereas in the citric acid medium, some labile compounds may had undergone hydrolysis or extraction. The oxygen content ranged from 11.15% to 13.78%. The highest values were observed in samples precipitated with citric acid, indicating a greater presence of oxygen-containing functional groups (carboxyl, phenolic, and quinonoid structures). At the same time, the lowest oxygen content was found in hydrochloric acid, possibly due to a lower degree of molecular polarization and better preservation of the original aromatic structures [13]. Finally, the sulfur content varied between 1.2% and 1.8%, with the highest values recorded in sulfuric acid, which may be related to the adsorption of sulfate ions or chemical transformations during coagulation. In samples precipitated with citric and ascorbic acids, the sulfur content was minimal, indicating a weak interaction of these acids with sulfur-containing components of HAs.

The yield of HAs is an important indicator of precipitation efficiency. The highest value was observed when using ascorbic acid (94.81%) indicating mild coagulation conditions and minimal degradation of the humic structure. A high yield was also recorded for sulfuric acid (93.08%) and hydrochloric acid (91.03%). In the case of citric acid, the yield was slightly lower (89.31%), which could be attributed to the solubility of humic compounds in weak organic acids.

Many studies reported that HA precipitation can be carried out at a pH of 1-2, as in this range they lose solubility due to the protonation of carboxyl and phenolic groups, charge reduction, and subsequent coagulation [14-16]. In this study, the final pH values of the solutions ranged from 1.47 to 2.01, confirming the effectiveness of this method. Additionally, an increase in all precipitation parameters was accompanied by a decrease in atomic ratios, which may be associated with a rise in the degree of condensation of the humic structure. This phenomenon can be explained by the fact that high atomic ratios (C/H, C/N) denote low aromaticity, while their decrease reflects a higher degree of aromatization and stabilization of condensed aromatic systems in HAs [17].

To further understand the influence of different acids on the structure of precipitated HAs, FTIR analysis was conducted. This method enabled the identification of key functional groups present in the HAs samples, as well as the structural changes occurring during precipitation. The FTIR spectra and corresponding peak tables are presented in Figures 2-5, and Tables II-V.

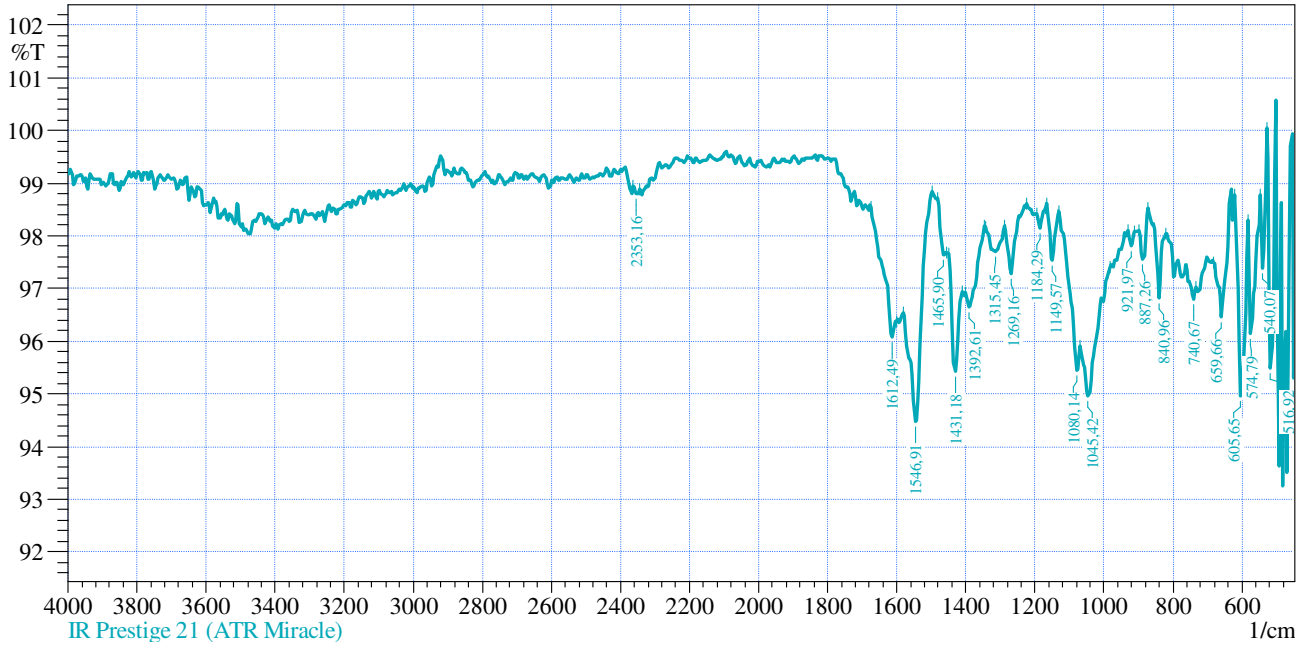

Fig. 2. IR spectrogram of HA precipitated with HCl.

TABLE II. PEAKS OF THE IR SPECTROGRAM OF HA PRECIPITATED WITH HCL

No.	Peak (cm^{-1})	Intensity	Corr. intensity	Base (H)	Base (L)	Area	Corr. area
1	516.92	95.486	3.8559	524.64	505.35	0.2722	0.2116
2	540.07	97.3856	1.9043	547.78	528.5	0.1346	0.0962
3	574.79	96.1374	2.1358	582.5	551.64	0.3821	0.145
4	605.65	94.9657	3.2832	621.08	586.36	0.5802	0.2934
5	659.66	96.4516	1.6031	682.8	636.51	0.5579	0.1723
6	740.67	96.8051	0.3205	759.95	732.95	0.3587	0.0224
7	840.96	97.5568	1.3977	867.97	821.68	0.4498	0.0887
8	887.26	97.5568	0.733	898.83	871.82	0.2421	0.0468
9	921.97	97.8144	0.2866	929.69	910.4	0.1732	0.0121
10	1045.42	94.9563	1.1951	1064.71	983.7	1.389	0.1785
11	1080.14	95.4562	0.9285	1103.29	1068.56	0.8542	0.0674
12	1149.57	97.532	0.9665	1165.0	1134.14	0.273	0.0685
13	1184.29	98.1562	0.3154	1195.87	1168.86	0.1954	0.0165
14	1269.16	97.2734	0.9632	1284.59	1222.87	0.5262	0.0884
15	1326.17	97.71	0.467	1342.46	1288.45	0.5035	0.0722
16	1392.61	96.648	0.4533	1400.32	1346.31	0.6459	0.0761
17	1431.18	95.4175	0.8803	1450.47	1411.89	0.6269	0.1617
18	1465.9	97.6488	0.4787	1481.33	1454.33	0.2502	0.0284
19	1546.91	97.4705	0.4033	1581.63	1496.76	1.3031	0.469
20	1612.49	96.0769	0.6406	1674.21	1600.92	0.9158	0.0778
21	2353.16	98.8085	0.0955	2364.73	2345.44	0.0962	0.0044

The analysis of the IR spectrum of HAs precipitated with hydrochloric acid allowed for the identification of the main functional groups involved in the chemical structure of humic compounds, as well as the characteristic changes induced by the precipitation process. In the 3400-3200 cm^{-1} region, absorption bands traditionally corresponding to hydroxyl (-OH) groups were observed, playing a crucial role in the formation of hydrogen bonds. However, their intensity may be reduced due to overlap with signals from N-H groups of amides or amines [18]. In this case, a broad, weakly expressed peak may indicate the presence of both hydroxyl and amide groups, confirming the presence of polar functional groups responsible for the high sorption activity of HAs. The characteristic absorption band in the 1750-1700 cm^{-1} region revealed the presence of carbonyl (C=O) and carboxyl (-COOH) groups, enhancing the acidic nature of humic substances. In this spectrum, distinct peaks at 1546.91 cm^{-1} and 1465.9 cm^{-1} were observed, implying a significant amount of carboxyl groups involved in acid-base reactions. Their high intensity checked the key role of carboxyl functional groups in metal complexation processes and interactions with the environment [19]. Pronounced peaks in the 1600-1400 cm^{-1} region (1612.49 cm^{-1}, 1546.91 cm^{-1}, 1465.90 cm^{-1}) demonstrated the presence of aromatic carbon bonds (C=C), which are characteristic of highly condensed HAs. The intensity of these bands suggested the dominance of the aromatic backbone in the structure of the compounds, verifying the high degree of aromaticity of humic substances. The bands in the 1200-1000 cm^{-1} region (1045.42 cm^{-1}, 1149.57 cm^{-1}) mentioned the presence of esters, phenolic, and alcoholic groups (-OH, C-O), as well as possible polysaccharide fragments. Their intensity may be associated with the presence of cellulose-like residues or lignin degradation products [20]. In the 900-600 cm^{-1} region (840.96 cm^{-1}, 740.67 cm^{-1}, 659.66 cm^{-1}), deformation vibrations of aliphatic (C-H) and aromatic groups were observed. Specifically, peaks in the 740-650 cm^{-1} range may be attributed to the presence of polycyclic aromatic systems or alkyl-substituted benzene rings.

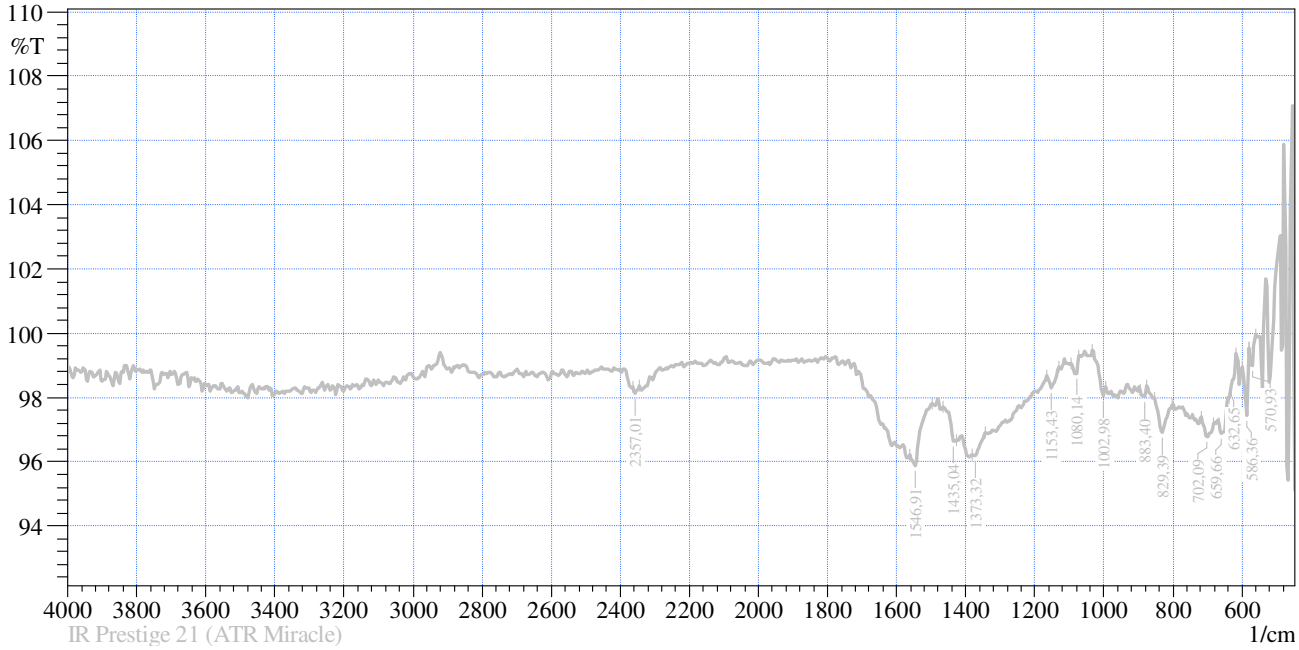

Fig. 3. IR spectrogram of HA precipitated with H_2SO_4.

TABLE III. PEAKS OF THE IR SPECTROGRAM OF HA PRECIPITATED WITH H_2SO_4

No.	Peak (cm^{-1})	Intensity	Corr. intensity	Base (H)	Base (L)	Area	Corr. area
1	570.93	98.994	0.724	578.64	559.36	0.044	0.027
2	586.36	97.416	1.905	597.93	578.64	0.135	0.077
3	632.65	97.977	0.277	636.51	617.22	0.108	0.01
4	659.66	96.884	0.532	667.37	644.22	0.292	0.045
5	702.09	96.762	0.54	717.52	682.8	0.466	0.05
6	829.39	96.907	0.987	852.54	802.39	0.575	0.108
7	883.4	98.028	0.281	894.97	875.68	0.157	0.014
8	1002.98	98.063	0.495	1033.85	995.27	0.212	0.026
9	1080.14	98.756	0.463	1095.57	1072.42	0.107	0.024
10	1153.43	98.298	0.469	1165.0	1130.29	0.222	0.041
11	1373.32	96.169	0.191	1381.03	1342.46	0.601	0.017
12	1435.04	96.625	0.254	1465.9	1427.32	0.472	-0.007
13	1546.91	95.883	0.704	1562.34	1496.76	0.899	0.034
14	2357.01	98.138	0.214	2364.73	2345.44	0.15	0.011

In Figure 3 and Table III, a broad signal in the 3400-3200 cm^{-1} region (not explicitly represented in numerical data but characteristic of HAs) indicated the presence of hydroxyl (-OH) groups and potential hydrogen bonding. This region suggested the presence of alcoholic and phenolic groups, as well as amine (-NH) groups, confirming the polar nature of humic compounds and their ability to form intermolecular interactions [21]. A distinct peak at 1546.91 cm^{-1} implies the presence of carbonyl (C=O) and carboxyl (-COOH) groups. This band highlighted the existence of oxygen-containing functional groups, which are crucial in acid-base interactions and complexation processes. Absorption bands in the 1600-1400 cm^{-1} region (1546.91 cm^{-1}, 1435.04 cm^{-1}, 1373.32 cm^{-1}) indicated the presence of aromatic C=C bonds. Bands in the 1200-1000 cm^{-1} range (1002.98 cm^{-1}, 1080.14 cm^{-1}, 1153.43 cm^{-1}) were associated with esters, phenolic groups, and alcohols (-OH, C-O, C-O-C). These functional groups are vital in the chemical reactivity of HAs and their ability to interact with metals [22]. Peaks in the 900-600 cm^{-1} region (883.40 cm^{-1}, 829.39 cm^{-1}, 702.09 cm^{-1}, 659.66 cm^{-1}) were related to deformation vibrations of aromatic carbons and alkyl substituents. This area validated the existence of polycyclic aromatic systems, enhancing the condensed structure of humic compounds. Compared to HAs precipitated with hydrochloric acid, the precipitation with sulfuric acid exhibited strong carbonyl (C=O) and carboxyl (-COOH) groups, which denoted more pronounced oxidative processes and additional interactions with sulfate ions. Additionally, a high intensity of aromatic C=C bonds was observed, developing a more condensed structure of HAs in this environment.

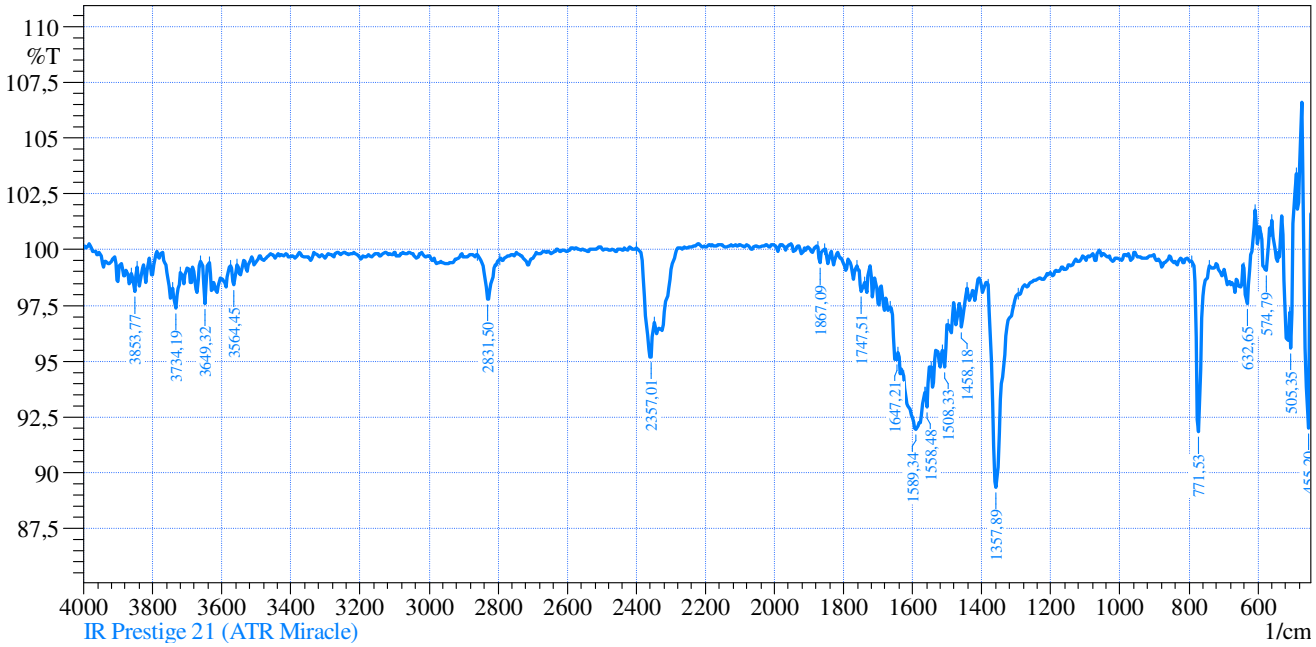

Fig. 4. IR spectrogram of HA precipitated with citric acid.

TABLE IV. PEAKS OF THE IR SPECTROGRAM OF HA PRECIPITATED WITH CITRIC ACID

No.	Peak (cm^{-1})	Intensity	Corr. intensity	Base (H)	Base (L)	Area	Corr. area
1	455.2	91.988	10.215	470.63	447.49	0.363	0.597
2	505.35	95.587	2.842	509.21	489.92	0.056	0.076
3	574.79	99.096	1.778	590.22	559.36	0.002	0.125
4	632.65	97.565	2.27	640.37	609.51	0.167	0.161
5	771.53	91.835	7.549	790.81	740.67	0.66	0.519
6	1357.89	89.385	8.941	1381.03	1296.16	1.968	1.305
7	1458.18	96.55	1.014	1462.04	1442.75	0.217	0.04
8	1508.33	93.01	1.074	1512.19	1496.76	0.29	0.022
9	1558.48	92.936	0.939	1562.34	1546.91	0.418	0.015
10	1589.34	91.974	1.882	1627.92	1566.2	2.029	0.349
11	1647.21	95.08	0.633	1666.5	1643.35	0.391	0.021
12	1747.91	93.013	0.663	1739.79	1739.79	0.014	0.022
13	1867.09	99.444	0.643	1874.81	1855.52	0.017	0.023
14	2357.01	95.17	2.087	2399.45	2349.3	0.548	0.194
15	2831.4	95.087	0.187	2858.51	2796.78	0.289	0.197
16	3564.45	95.423	0.956	3576.92	3556.74	0.129	0.073
17	3649.32	95.667	1.873	3660.89	3637.75	0.123	0.073
18	3734.19	97.389	1.126	3741.9	3718.76	0.188	0.055
19	3853.77	98.121	0.95	3861.49	3846.06	0.088	0.022

In Figure 4 and Table IV, absorption bands in the 3800-3600 cm^{-1} area (3649.32 cm^{-1}, 3734.19 cm^{-1}, 3853.77 cm^{-1}) revealed the existence of hydroxyl (-OH) and amine (-NH) groups. The high intensity of these bands suggested a significant presence of phenolic and alcoholic groups, highlighting the active involvement of HAs in hydrogen bonding. A pronounced band at 1747.91 cm^{-1} confirmed the presence of carbonyl (C=O) and carboxyl (-COOH) functional groups. Bands in the 1600-1400 cm^{-1} region (1589.34 cm^{-1}, 1558.48 cm^{-1}, 1508.33 cm^{-1}, 1458.18 cm^{-1}) indicated the presence of aromatic C=C bonds. The presence of distinct bands in the 1200–1000 cm^{-1} region (1080.14 cm^{-1}, 1002.98 cm^{-1}) indicates phenolic and ether (C-O, C-O-C) groups, which play an essential role in the chemical reactivity of HAs. Peaks in the 900–600 cm^{-1} region (771.53 cm^{-1}, 632.65 cm^{-1}, 505.35 cm^{-1}) corresponded to deformation vibrations of aromatic carbons and alkyl substituents [23]. The high intensity of these signals confirms the presence of condensed aromatic systems, indicating a high degree of polymerization of humic compounds.

Compared to HAs precipitated with hydrochloric and sulfuric acids, humic substances precipitated with citric acid exhibited more pronounced hydroxyl and carbonyl groups, representing a lower degree of degradation and a higher preservation of oxygen-containing compounds.

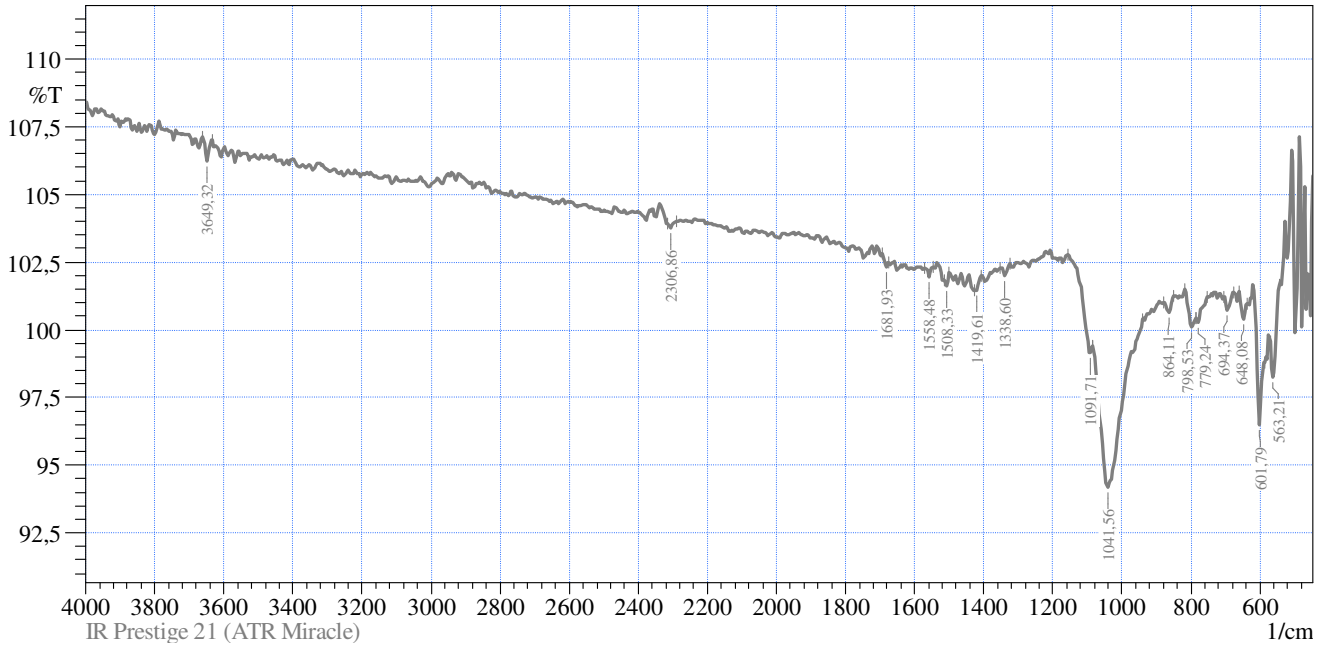

Fig. 5. IR spectrogram of HA precipitated with ascorbic acid.

TABLE V. PEAKS OF THE IR SPECTROGRAM OF HA PRECIPITATED WITH ASCORBIC ACID

No.	Peak (cm^{-1})	Intensity	Corr. intensity	Base (H)	Base (L)	Area	Corr. area
1	563.21	98.262	1.893	570.93	543.93	0.031	0.12
2	601.79	96.492	3.645	617.22	586.36	0.247	0.241
3	648.08	100.408	0.785	659.66	636.51	-0.078	0.042
4	694.37	100.723	0.563	705.95	675.09	-0.144	0.04
5	779.24	100.258	0.362	786.96	752.24	-0.105	0.019
6	798.53	100.112	0.729	817.82	786.96	-0.079	0.051
7	864.11	100.643	0.48	879.54	848.68	-0.12	0.029
8	1041.56	94.207	5.492	1083.99	941.26	7.104	1.646
9	1091.71	99.14	0.268	1157.29	1083.99	-0.39	-0.046
10	1338.6	102.01	0.35	1354.03	1323.17	-0.297	0.016
11	1419.61	101.45	0.293	1427.32	1408.04	-0.137	0.007
12	1508.33	101.638	0.29	1512.19	1500.62	-0.09	0.007
13	1558.48	101.953	0.341	1570.06	1546.91	-0.217	0.011
14	1681.93	102.315	0.299	1693.5	1674.21	-0.208	0.011
15	2306.86	103.771	0.194	2314.58	2291.43	-0.383	0.008
16	3649.32	106.244	0.84	3660.89	3633.89	-0.76	0.042

In Figure 5 and Table V, bands in the 1700-1500 cm^{-1} region (1681.93 cm^{-1}, 1558.48 cm^{-1}, 1508.33 cm^{-1}) implied the presence of carbonyl (C=O) and carboxyl (-COOH) functional groups. Additionally, absorption bands in the 1600-1400 cm^{-1} area (1558.48 cm^{-1}, 1508.33 cm^{-1}, 1419.61 cm^{-1}) corresponded to aromatic carbon (C=C) bonds. The 1200-1000 cm^{-1} range (1091.71 cm^{-1}, 1041.56 cm^{-1}) suggested the presence of phenolic and ether (C-O, C-O-C) groups, as well as complex

hydrocarbon structures. Peaks in the 900-600 cm^{-1} region (779.24 cm^{-1}, 694.37 cm^{-1}, 648.08 cm^{-1}, 601.79 cm^{-1}) were associated with deformation vibrations of aromatic rings and alkyl substituents [24].

The results of the IR spectroscopic analysis demonstrated that the precipitation of HAs with different acids significantly affected their chemical structure, functional composition, and degree of aromaticity, as illustrated in Figure 6.

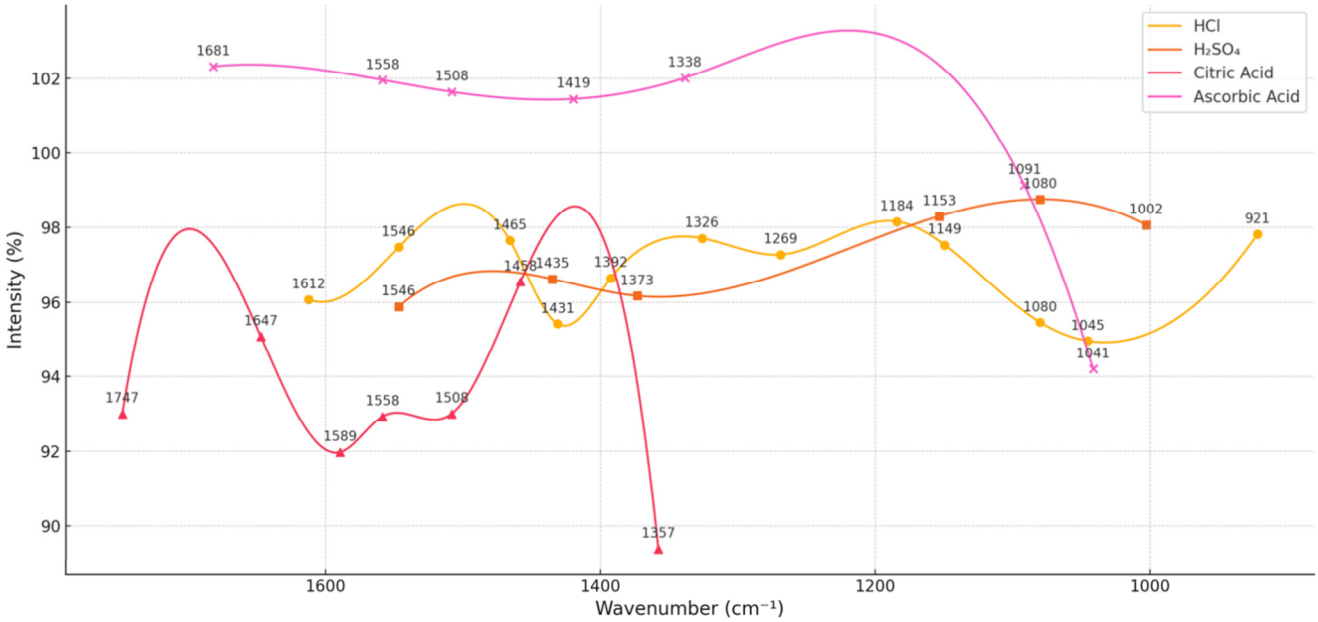

Fig. 6. IR spectra of HA precipitated with different acids (900-1700 cm^{-1}).

Hydrochloric and sulfuric acids promoted the formation of more condensed and aromatic structures, as evidenced by high-intensity absorption bands corresponding to C=C bonds in aromatic systems. At the same time, citric and ascorbic acids provided better preservation of hydroxyl (-OH) and phenolic (-C-OH) groups, making HAs precipitated with these acids more polar and reactive. Sulfuric acid exhibited the strongest influence on the presence of carboxyl groups, confirmed by the pronounced carbonyl absorption bands. This made HAs precipitated with sulfuric acid more suitable for sorption processes and acid-base interactions. In contrast, the precipitation with ascorbic acid demonstrated high intensity in phenolic and ether groups, revealing preservation of oxygen-containing compounds and enhanced complexation ability. The deformation vibrations of aliphatic and aromatic structures were most pronounced in HAs precipitated with hydrochloric and sulfuric acids, suggesting a higher degree of polymerization and condensation of these compounds. Conversely, HAs precipitated with citric and ascorbic acids showed lower aromatic condensation, making them more polar and reactive in chemical interactions.

Thus, the choice of acid for the process of HAs precipitation depended on the desired properties of the final product. Mineral acids (HCl and H_2SO_4) contributed to the formation of more stable and aromatic compounds, making them promising for sorption and adsorption processes. On the other hand, organic acids (citric and ascorbic acids) preserved oxygen-containing functional groups, enhancing the chemical activity of humic substances and making them valuable for biochemical and environmental applications.

The utilization of mineral acids for HAs precipitation has been a well-studied and widely applied method [25]. At the same time, there is very little information available regarding the use of organic acids in this process.

Compared to other studies, the observed increase in aromaticity and C=C signal intensities for HAs precipitated with mineral acids is consistent with the findings of [16], where similar aromatic condensation occurred during acid treatment of lignite-derived HAs. Likewise, authors in [15] noted that harsher chemical conditions tend to enhance the polymerization and stability of humic structures. In contrast, these results for citric and ascorbic acid precipitation align with those of [25], where it was observed that organic acids preserved more oxygenated functional groups during plant-based extractions. The relatively higher O content and lower aromaticity in the organic acid treatments further supported this trend, suggesting that these acids may offer advantages, where high polarity and sorption reactivity are desired (e.g., in soil remediation or metal ion complexation applications.)

In [26], a method for obtaining rutin-enriched extracts from plant raw materials using organic acids, including ascorbic and citric acids was described. Additionally, authors in [27] discussed modern extraction methods, entailing the use of organic acids for obtaining functional ingredients from plant materials, highlighting their use as effective agents in extraction and purification processes. In another study the employment of citric acid in various biomaterials and its role in coagulation and structural formation processes was examined [28]. The authors noted that citric acid can participate in the

formation of network structures and influence material properties. Despite the limited data on the direct precipitation of HAs using citric and ascorbic acids, existing studies indicated their significant potential, making the proposed method well-founded and promising.

IV. CONCLUSION

This study provided a comparative analysis of Humic Acid (HA) precipitation from brown coal waste using both mineral (hydrochloric and sulfuric) and organic (citric and ascorbic) acids. Fourier Transform Infrared (FTIR) spectroscopy and CHN elemental analysis were performed. The results revealed that the highest HA yield was obtained with ascorbic acid (94.81%), followed by sulfuric (93.08%), hydrochloric (91.03%), and citric acid (89.31%). The CHN analysis revealed that acid type significantly influenced the chemical structure, aromaticity, and functional group composition of the resulting HAs. Mineral acids promoted greater aromatic condensation, as evidenced by strong C=C absorption bands, while organic acids preserved more hydroxyl and carboxyl groups, enhancing polarity and potential reactivity.

The novelty of this work lies in the systematic comparison of organic and mineral acid precipitation of HAs, an area that remains underexplored in current literature. The study demonstrated that citric and ascorbic acids can serve as viable, environmentally friendly alternatives for HA precipitation, particularly when the preservation of reactive functional groups is desired for applications, such as metal ion complexation, soil remediation, and bioavailable carbon enrichment. Future research should focus on optimizing the concentration and pH conditions for organic acid precipitation, assessing the sorption performance and environmental behavior of the resulting HAs, and exploring potential scale-up and industrial applications for converting coal waste into value-added humic materials.

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REFERENCES

[1] A. Maffia, M. Oliva, F. Marra, C. Mallamaci, S. Nardi, and A. Muscolo, "Humic Substances: Bridging Ecology and Agriculture for a Greener Future," *Agronomy*, vol. 15, no. 2, Feb. 2025, Art. no. 410, https://doi.org/10.3390/agronomy15020410.

[2] W. Machado, J. C. Franchini, M. De Fátima Guimarães, and J. T. Filho, "Spectroscopic characterization of humic and fulvic acids in soil aggregates, Brazil," *Heliyon*, vol. 6, no. 6, Jun. 2020, Art. no. e04078, https://doi.org/10.1016/j.heliyon.2020.e04078.

[3] M. A. Proskurnin, D. S. Volkov, and O. B. Rogova, "Temperature Dependences of IR Spectral Bands of Humic Substances of Silicate-Based Soils," *Agronomy*, vol. 13, no. 7, Jul. 2023, Art. no. 1740, https://doi.org/10.3390/agronomy13071740.

[4] Y. Mikhaylova, G. Adam, L. Häussler, K.-J. Eichhorn, and B. Voit, "Temperature-dependent FTIR spectroscopic and thermoanalytic studies of hydrogen bonding of hydroxyl (phenolic group) terminated hyperbranched aromatic polyesters," *Journal of Molecular Structure*, vol. 788, no. 1, pp. 80–88, May 2006, https://doi.org/10.1016/j.molstruc.2005.11.020.

[5] M. Schnitzer and S. U. Khan, *Soil Organic Matter*, 1st ed., vol. 8. Amsterdam, Netherlands: Elsevier, 1975.

[6] F. J. Stevenson and K. M. Goh, "Infrared spectra of humic acids and related substances," *Geochimica et Cosmochimica Acta*, vol. 35, no. 5, pp. 471–483, May 1971, https://doi.org/10.1016/0016-7037(71)90044-5.

[7] F. J. Stevenson and K. M. Goh, "Infrared spectra of humic acids and related substances," *Soil Science*, vol. 117, no. 1, Jan. 1974, Art. no. 34.

[8] P. Vinkler, B. Lakatos, and J. Meisel, "Infrared spectroscopic investigations of humic substances and their metal complexes," *Geoderma*, vol. 15, no. 3, pp. 231–242, Mar. 1976, https://doi.org/10.1016/0016-7061(76)90077-X.

[9] X. Yang *et al.*, "Solubility characteristics of soil humic substances as a function of pH." Copernicus Publications Göttingen, Germany, 2024, https://doi.org/10.5194/egusphere-2023-2994.

[10] B. Smailov and U. Aravind, "Synthesis of humic acid with the obtaining of potassium humate based on coal waste from the Lenger deposit, Kazakhstan," *Green Processing and Synthesis*, vol. 13, no. 1, Jan. 2024, https://doi.org/10.1515/gps-2023-0150.

[11] *Brown coals and lignites-Determination of humic acids*, ISO 5073, 1985.

[12] K. A. Thorn and L. G. Cox, "N-15 NMR spectra of naturally abundant nitrogen in soil and aquatic natural organic matter samples of the International Humic Substances Society," *Organic Geochemistry*, vol. 40, no. 4, pp. 484–499, Apr. 2009, https://doi.org/10.1016/j.orggeochem.2009.01.007.

[13] V. D. Tikhova, T. F. Bogdanova, V. P. Fadeeva, and V. N. Piottukh-Peletsky, "Study of the fragment composition of humic acids of different origin using IR-EXPERT software," *Journal of Analytical Chemistry*, vol. 68, no. 1, pp. 86–94, Jan. 2013, https://doi.org/10.1134/S1061934813010139.

[14] E. Vjalykh and S. Ilarionov, "Humic acid synthesis method," Russian Federation Patent No. RU2430075C1, 2011.

[15] G. Cheng, Z. Niu, C. Zhang, X. Zhang, and X. Li, "Extraction of Humic Acid from Lignite by KOH-Hydrothermal Method," *Applied Sciences*, vol. 9, no. 7, Jan. 2019, Art. no. 1356, https://doi.org/10.3390/app9071356.

[16] M. Stefanova, L. Gonsalvesh, S. Marinov, J. Czech, R. Carleer, and J. Yperman, "Reductive pyrolysis of Miocene-aged lignite humic acids, Bulgaria," *Fuel*, vol. 165, pp. 324–330, Feb. 2016, https://doi.org/10.1016/j.fuel.2015.10.032.

[17] E. H. Novotny *et al.*, "Studies of the Compositions of Humic Acids from Amazonian Dark Earth Soils," *Environmental Science & Technology*, vol. 41, no. 2, pp. 400–405, Jan. 2007, https://doi.org/10.1021/es060941x.

[18] S. Siggia and J. G. Hanna, "Quantitative organic analysis via functional groups. Moscow," *Chemistry*, pp. 132–135, 1983.

[19] L. Li, L. Ma, Y. Lu, Y. Wang, and S. Sun, "Spectroscopic Analysis of the Effects of Alkaline Extractants on Humic Acids Isolated from Herbaceous Peat," vol. 39, pp. 20–25, Mar. 2024.

[20] U. Fooken and G. Liebezeit, "An IR study of humic acids isolated from sediments and soils," *Senckenbergiana maritima*, vol. 32, no. 1, pp. 183–189, Jul. 2003, https://doi.org/10.1007/BF03043094.

[21] T. Fischer, "Humic supramolecular structures have polar surfaces and unpolar cores in native soil," *Chemosphere*, vol. 183, pp. 437–443, Sep. 2017, https://doi.org/10.1016/j.chemosphere.2017.05.125.

[22] A. Ohta, H. Kagi, H. Tsuno, M. Nomura, T. Okai, and N. Yanagisawa, "IR and XANES spectroscopic studies of humic acids reacting with Cr(III) and Cr(VI)," *Geological Survey Research Report*, vol. 62, no. 9–10, pp. 347–355, Dec. 2011, https://doi.org/10.9795/bullgsj.62.347.

[23] S. B. Reddy, M. S. Nagaraja, G. G. Kadalli, and B. V. Champa, "Fourier Transform Infrared (FTIR) Spectroscopy of Soil Humic and Fulvic Acids Extracted from Paddy Land Use System," *International Journal of Current Microbiology and Applied Sciences*, vol. 7, no. 5, pp. 834–837, 2018.

[24] J. Niemeyer, Y. Chen, and J.-M. Bollag, "Characterization of Humic Acids, Composts, and Peat by Diffuse Reflectance Fourier-Transform Infrared Spectroscopy," *Soil Science Society of America Journal*, vol. 56, no. 1, pp. 135–140, 1992, https://doi.org/10.2136/sssaj1992.03615995005600010021x.

[25] B. F. Zimmermann and M. Gleichenhagen, "The effect of ascorbic acid, citric acid and low pH on the extraction of green tea: How to get most out of it," *Food Chemistry*, vol. 124, no. 4, pp. 1543–1548, Feb. 2011, https://doi.org/10.1016/j.foodchem.2010.08.009.

[26] K. Minami, S. Taniwaki, and A. Katsumata, "Rutin-rich extract and method of making same," US Patent US9827262B2, 2017.

[27] N. Mahato, M. Sinha, K. Sharma, R. Koteswararao, and M. H. Cho, "Modern Extraction and Purification Techniques for Obtaining High Purity Food-Grade Bioactive Compounds and Value-Added Co-Products from Citrus Wastes," *Foods*, vol. 8, no. 11, Nov. 2019, Art. no. 523, https://doi.org/10.3390/foods8110523.

[28] H. Xu *et al.*, "Citric Acid: A Nexus Between Cellular Mechanisms and Biomaterial Innovations," *Advanced Materials*, vol. 36, no. 32, 2024, Art. no. 2402871, https://doi.org/10.1002/adma.202402871.