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Obtaining Humic Acids with the Required Structure-Group Composition from Brown Coals

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Abstract

The samples of native and *n*-butanol-modified humic acids isolated from brown coals of the Kansk-Achinsk and South Ural coal basins (Russia) were obtained. Their composition and properties were characterized using the methods of elemental, spectral, technical analysis and testing for biological activity. Changes in the structural group parameters of modified humic acids were revealed by means of ^{13}C NMR (CPMAS), IR and Raman spectroscopy. The biological activity of native and modified humic acids was evaluated by means of phytotesting with the seeds of Iren wheat. It is shown that modified humic acids are characterized by increased biological activity. This is due to an increase in the relative content of aromatic structural fragments, which is accompanied by an increase in aromaticity index f_a and the ratio of aromaticity to aliphaticity $f_{ar/al}$ of humic acids.

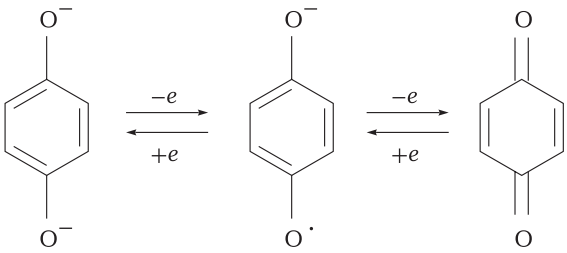
Keywords: brown coal, humic acid, modification, biological activity, index of phytoactivity

INTRODUCTION

The modern stage of scientific and technological progress is connected with an increase in reasonableness and efficiency of the use of natural and energy resources. At this stage, brown coal may serve not only as a low-quality fuel but also as a rich source of relevant products of coal chemistry, in particular humic substances (HS) – raw material which is widely used in industry and especially in agriculture as a highly efficient stimulator of plant growth.

The reasonableness and efficiency of the use of HS may be enhanced by increasing their biological activity. There is no doubt that the nature of the biological activity of HS is essentially connected with the features of their structural group composition. In a series of works with the seeds of wheat and radish, a direct significant correlation was established between the biological activity of humic acids (HA) from different samples of brown coal and structural group parameters calculated from the data of ^{13}C NMR spectroscopy (CPMAS): aromaticity degree (f_a, $R^2 = 0.9$), hydrophilic/hydrophobic properties ($f_{h/h}$, $R^2 = 0.9$), and aromaticity/aliphaticity ($f_{ar/al}$, $R^2 = 0.9$), where R^2 is determination coefficient [1–4]. It is assumed that the indicated structural group parameters depict the content of phenol hydroxyl groups (C_{ar}–OH) in HA, able to participate in oxidation-reduction reactions in a plant cell and enhance these processes according to Bakh – Paladin – Szent-Gyorgyi theory [5]. Quinones are formed as a result of enzymatic dehydrogenase-driven oxidation of phenols through intermediate compounds of the type of semiquinones (Scheme 1).

The field tests of HA from brown coal of the Kans-Achinsk and Southern Ural basins in the form of 0.005 % solutions of sodium humate (HumNa) under the conditions of fertile soil and technogenic landscapes of the Zarechniy open-pit coal mine of JSC SUEK-Kuzbass showed that in the case of sufficient soil wetting there is a significant correlation between the biological activity of HA with respect to wheat and radish and the f_a parameter [6]. However, under the condi-



Scheme 1.

tions of insufficient wetting, the most clearly pronounced correlation is that between the phase parameters of wheat seedlings with the $f_{h/h}$ parameter of HA of these coal samples. So, to enhance the reasonableness and efficiency of the application of HA, it is necessary to use the procedures of purposeful action on their structural group composition.

The structural group composition of HS may be affected by changing the conditions of the extraction of these substances. We demonstrated in [1] that under the variation of the conditions of HA extraction (the concentration of NaOH solution, 1–5 %; temperature, 25–98 °C; duration of extraction, 5–5.5 h) from brown coal of the Kansk-Achinsk coal basin one may change the structural group composition significantly, according to the data of ^{13}C NMR spectroscopy. Within the indicated range of variation, HA with f_a varying from 39.9 to 65.7 and phytoactivity index (PI) from 1.09 to 1.25 with respect to wheat seeds were obtained.

A promising direction of the effect on the structural group composition of HA is the modification of oxygenated functional groups of initial coal through alkylation with alcohols for the purpose of increasing their reactivity by destroying intermolecular interactions in the organic mass of coal (OMC) [7]. The use of alkylation, especially O-alkylation of young solid fossil fuel (SFF) containing a large amount of oxygenated functional groups, leads to depolymerization of their structure. This affects both the quantitative yield of extraction products and their composition and properties. It was demonstrated in [7, 8] that alkylation of the organic matter of brown coal with C_1–C_5 alcohols in the presence of strong protonic acids leads to an increase in the yield of bitumen species. The highest bitumen yield is achieved in the case when butanol is used. In addition to an increase in bitumen yield, it was determined that SFF alkylation with butanol leads to changes in the structural group composition of the extracted HA, namely to an increase in f_a and $f_{ar/al}$ values as a consequence of the transition of some aliphatic fragments into the solution at the stage of the destruction of the organic mass of coal during modification. So, the directed chemical modification of initial brown coal followed by the separation of bitumen allows affecting the structural group composition and the properties of HA extracted from residual coal.

In this connection, the studies aimed at the revelation of the possibility of a directed effect on the structural group composition of HA through their direct chemical modification after the extraction from the raw material cause interest.

The goal of the present work was to study the effect of *n*-butanol modification of HA extracted from brown coal on the structural group composition and biological activity.

EXPERIMENTAL

Materials

Brown coal samples from the Tisul deposit of the Kansk-Achinsk basin (Kaychakskiy region (BUTS) and the form oxidized in the bed (BUTSO)) and from the Tyulganskoye deposit of the Southern Ural basin (BUT) were used as the initial raw material (Table 1).

Investigation procedures

For alkylation, a portion of HA (5 g) was dissolved in 100 ml of *n*-butyl alcohol, acidified with hydrochloric acid to pH 2–3, and boiled for 3 h at butanol boiling point, then cooled to room temperature. The resulting mixture was diluted with 2 L of distilled water. The precipitate was separated by filtering through a Buchner funnel, washed with a large amount of water, and dried to the constant mass.

To establish a connection between the structural group composition and biological activity of HA, tests were carried out according to the procedure described in GOST 12038–84 [9] with the seeds of Iren wheat in the form of HumNa solutions (0.005 % concentration). The biological activity of HA was evaluated from the integral phytoactivity index (PI) taking into account three test functions [10]: the seed germination energy (GE), root length (RL) and seedling height (SH). The PI value is calculated as the arithmetic mean of the sum of GE, SH and RL for the seeds (in % to the reference) expressed in the fractions of unity:

$$PI = \frac{(GE + SH + RL)}{3 \cdot 100}$$

TABLE 1

Data of technical and elemental analyses of brown coal samples and the extracted humic acids (HA)

Sample	W^a, %	A^d, %	V^{daf}, %	Elemental composition, mass %					H/C atomic ratio	$(HA)_t^{daf}$, (HumNa), %
				C^{daf}	H^{daf}	O_d^{daf}	N^{daf}	S_t^a		
BUTS	8.1	6.1	48.1	64.3	4.7	26.9	0.7	4.4	0.9	22.3
HA HumNa BUTS	4.9	3.2	–	59.1	4.9	32.6	0.7	3.7	1.0	–
BUTSO	10.0	43.5	80.3	69.3	6.0	23.6	0.8	0.6	1.0	60.9
HA HumNa BUTSO	10.6	10.9	–	59.8	6.2	33.0	0.8	0.4	1.2	–
BUT	6.5	23.5	67.3	66.2	7.0	25.8	0.8	0.5	1.3	39.1
HA HumNa BUT	3.6	7.6	–	62.9	5.8	30.2	0.9	0.4	1.1	–

Notes. 1. daf – dry ash-free state of the sample; d – dry state of the sample; W^a – analytical humidity according to GOST R 52917–2008; A^d – ash content per dry sample according to GOST 11022–95; V^{daf} – content of volatile substances according to GOST 6382–2001; C, H, N – element content according to GOST 2408.1–95 (Liebig's method) and GOST 28743–93; O_d – oxygen content (calculated) according to GOST 2408.3–95; S_t^a – total sulphur content according to GOST 8606–2015; $(HA)_t^{daf}$ – the yield of free humic acids according to GOST 9517–94; HumNa – sodium humate. 2. Measurement error: not more than 2 %. 3. Dash – not determined.

The experiment was repeated three times: three trays with 50 wheat or radish seeds in each for each kind of HA and the same with wetting with distilled water (reference, PI = 1.0).

Investigation methods

High-resolution solid-state ^{13}C NMR spectra were recorded with the help of an AVANCE III 300 WB instrument (Bruker, Germany) at a frequency of 75 MHz using a standard procedure of cross-polarization and magic angle spinning (CPMAS).

HA were characterized using three parameters calculated according to the data of ^{13}C NMR spectroscopy [11–13]:

1) aromaticity degree (f_a) depicts the content of aromatic groups, in particular, phenol: $f_a = C_{Ar-O} + C_{Ar}$;

2) aromaticity/aliphaticity ($f_{ar/al}$) shows the ratio of the content of aromatic carbon atoms to the content of aliphatic carbon atoms: $f_{ar/al} = (C_{Ar-O} + C_{Ar})/(C_{O-Alk-O} + C_{Alk-O} + C_{Alk})$;

3) the ratio of hydrophilic/hydrophobic properties ($f_{h/h}$) defines the ratio of oxygenated groups: $f_{h/h} = (C_{C=O} + C_{COOH(R)} + C_{Ar-O} + C_{O-Alk-O} + C_{Alk-O})/(C_{Ar} + C_{Alk})$, where C values are the integral intensities of the corresponding spectral regions of the samples.

IR spectra were recorded in tablets with KBr using an Infralyum FT-801 IR Fourier Transform spectrometer. Spectra were interpreted according to the data reported in [14].

Raman spectra were recorded with the help of an InVia Basis spectrometer (Renishaw, Great Britain) at the wavelength of 514.5 nm with the light spot diameter of ≤2 μm using a diffraction grating with 1800 strokes per 1 mm. Measurements were carried out within the spectral range of Raman shift 100–4000 cm^{-1}.

RESULTS AND DISCUSSION

Butanol-alkylated HA (HA-Bu) differ from initial HA samples by an increased content of aromatic carbon atoms (C_{Ar-O} and C_{Ar}) and decreased content of carbon atoms in aliphatic groups ($C_{O-Alk-O} + C_{Alk-O} + C_{Alk}$) (Table 2).

The samples of HA and HA-Bu are characterized by typical absorption bands in the IR spectra (Table 3). A broad band at 3650–3200 cm^{-1} is due to the stretching vibrations of O–H groups connected through hydrogen bonds; the bands within the range of 3000–2840 and 1470–1420 cm^{-1} are due to the stretching and bending vibrations of C–H bonds in CH_2 and CH_3 groups; 1750–1710 cm^{-1} – stretching vibrations of C=O bonds in carboxylic acids; 1690–1600 cm^{-1} – stretching vibrations of aromatic C=C bonds and double C=C bonds forming a linear polyconjugation system; 1330–1050 cm^{-1} – vibrations of C–O bonds in carboxylic acids, esters, O–H of phenols; 1260–970 cm^{-1} – vibrations of C–O bonds in alcohols. In the IR spectra of HA-Bu, the intensities of absorption bands within the ranges of 1750–1710, 1690–1610, 1330–1050 and 1260–970 cm^{-1} remain high, while the intensities of absorption bands within the regions 3650–3200, 3000–2840, 1470–1420 cm^{-1} decrease. This is the evidence of a decrease in the content of aliphatic fragments in HA-Bu (see Table 3), which agrees with the data

TABLE 2

Integral intensities of spectral regions for HA and HA-Bu samples according to the data of ^{13}C NMR spectroscopy (%) and calculated structural parameters

Sample	Chemical shift, ppm							Structural parameter		
	220–187 C=O	187–165 COOH(R)	165–145 C_{Ar-O}	145–108 C_{Ar}	108–90 $C_{O-Alk-O}$	90–48 C_{Alk-O}	48–5 C_{Alk}	f_a	$f_{h/h}$	$f_{ar/al}$
					BUTS					
HA	4.4	7.3	5.4	17.9	3.6	10.8	50.7	23.3	0.5	0.4
HA-Bu	1.0	9.7	7.9	34.2	10.7	10.7	36.4	42.1	0.4	0.9
					BUTSO					
HA	3.5	7.4	8.2	32.7	6.3	14.8	26.8	40.9	0.7	0.9
HA-Bu	0.8	5.3	15.2	37.6	13.1	13.1	28.1	52.8	0.5	1.3
					BUT					
HA	4.3	7.9	6.8	22.5	4.9	16.3	36.5	29.3	0.7	0.5
HA-Bu	0.7	6.5	7.5	28.4	14.2	14.2	42.8	35.9	0.4	0.6

Note. 1. HA, HA-Bu are initial HA and HA activated with butanol, respectively. 2. Relative error of the measurement of signal intensity is ±0.3 %.

TABLE 3

Characterization of IR absorption spectra of HA and HA-Bu

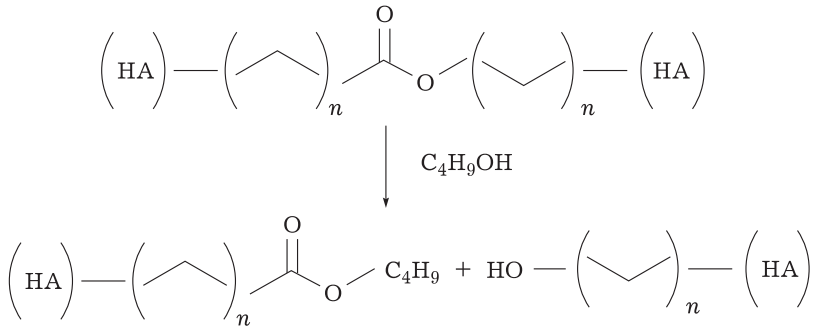
Sample	Wavenumber, cm^{-1}
HA BUTS	3376 (s, b), 2917 (s), 2850 (m), 1710 (s), 1610 (s), 1420 (m, b), 1257 (s, b)
HA-Bu BUTS	3390 (w, b), 2958 (m), 2933 (m), 2873 (m), 1721 (s), 1610 (s), 1460 (m), 1253 (s)
HA BUTSO	3375 (s, b), 2933 (s, b), 2850 (m), 1709 (s), 1614 (s), 1420 (m, b), 1240 (s, b)
HA-Bu BUTSO	3367 (w, b) 2956 (m), 2932 (m), 2871 (m), 1713 (s), 1614 (s), 1453 (m), 1273 (s, b)
HA BUT	3390 (s, b), 2918 (s), 2849 (m), 1712 (s), 1621 (s), 1417 (m, b), 1262 (s, b), 1032 (s)
HA-Bu BUT	3390 (w, b) 2957 (m), 2930 (m), 1725 (s), 1604 (m), 1462 (m), 1271 (s, b), 1033 (s)

Note. Characterization of absorption bands: s –strong, m – medium, w – weak, b – broad.

of ^{13}C NMR spectroscopy (see Table 2). Correspondingly, the relative content of aromatic fragments increases.

This dependence is also traced in the results of Raman spectroscopy. Alkylation of HA in BUTSO leads to a decrease in the ratio of band intensities I_D/I_G: for HA BUTSO – 0.794, for HA-Bu BUTSO – 0.480. This is the evidence of a decrease in the content of carbon atoms in sp^3-hybridization (D band) with an increase in the number of carbon atoms in sp^2-hybridization (G band). So, HA alkylation causes a decrease in the content of long-chain alkyl carbon atoms, and the structure of HA-Bu becomes more compact.

The detected changes are explained by re-esterification proceeding during HA alkylation with butanol in the presence of HCl as a catalyst: a heavy aliphatic alcohol fragment (radical) of an ester in the organic mass of HA is substituted by butyl according to equation [7] (Scheme 2).



Scheme 2.

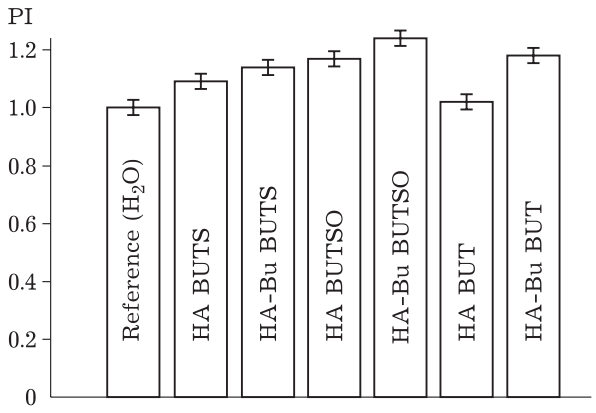


Fig. 1. Effect of alkylation with butanol on phytoactivity index (PI) of HA.

As a result, the HA molecule is depolymerized as a consequence of the transition of aliphatic alcohol fragments into solution. These fragments do not precipitate together with HA-Bu but remain in solution and form butanol extract thus getting separated. The organic mass of HA-Bu loses some amount of aliphatic fragments and becomes more aromatic in its nature.

Initial HA and HA-Bu samples were tested for biological activity with respect to the seeds of Iren wheat in the form of HumNa solutions (0.005 %). It was established that their biological activity increases as a result of HA modification (Fig. 1).

This is connected with an increase in the relative content of aromatic fragments, which is accompanied by an increase in f_a and $f_{ar/al}$ of HA samples after modification. The results of tests confirmed the direct correlation of f_a ($R^2 = 0.8$) and $f_{ar/al}$ ($R^2 = 0.9$) with the biological activity of HA (Fig. 2). These calculated structural group parameters depict the content of phenol hydroxyl groups in HA that are able to participate in oxidation-reduction reactions in a plant cell and enhance these processes according to Bakh–Paladin–Szent-Gyorgyi theory [5].

In each case, modification has a positive effect on the biological activity of HA. The highest biological activity is exhibited by initial HA and modified samples (HA-Bu) from naturally oxidized brown coal from the Tisul deposit (BUTSO) (see Fig. 1).

CONCLUSION

It is demonstrated that butanol alkylation of HA from brown coal of the Kansk-Achinsk and Southern Ural basins leads to an increase in the content of aromatic carbon atoms in their composition. These changes are confirmed by the results of ^{13}C NMR, IR and Raman spectroscopy. It was established that the biological activity of HA depends on the degree of aromaticity f_a and the relative content of aromatic and aliphatic fragments $f_{ar/al}$ of the organic mass of HA. The described procedure of modification through alkylation allows obtaining HA with increased biological activity, close in composition to highly active natural HA of naturally oxidized coal of the brown-coal stage of maturity.

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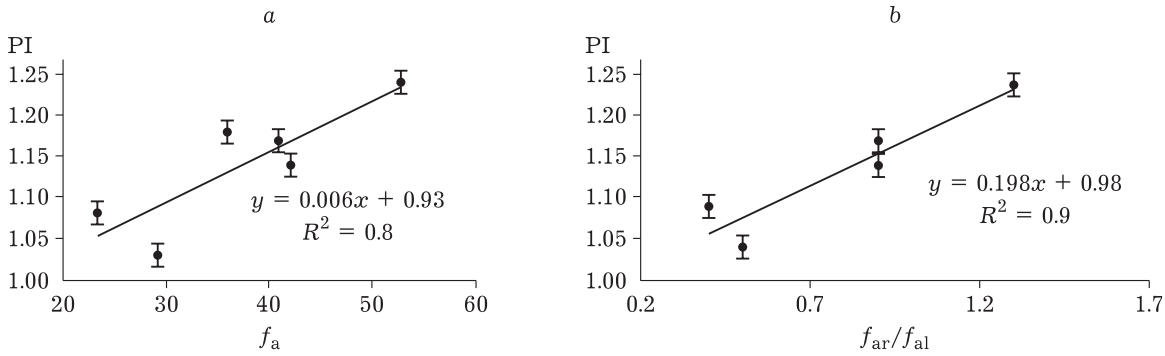

Fig. 2. Dependence of phytoactivity index (PI) of HA and HA-Bu samples on structural parameters: aromaticity degree f_a (*a*) and $f_{ar/al}$ (*b*).

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