UDC 662.73+547.992.2

DOI: 10.15372/KhUR2021338

Investigation on Humic Acids of the Shivee-Ovoo and Ulaan-Ovoo Coal in Mongolia

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Abstract

Humic acids are highly oxidized organic compounds originated from plants and coals. Therefore, the coals of the Shivee-Ovoo and Ulaan-Ovoo deposits were analyzed by proximate, ultimate, and FTIR spectroscopic analysis. It was confirmed that the Shivee-Ovoo coal is a low-rank lignite coal of B2 mark, and the Ulaan-Ovoo coal is subbituminous coal. So, they are suitable raw materials for obtaining humic acids. The yield of humic acids from the Shivee-Ovoo coal is 23.2 % and their solubility in water is 78.05 %. The yield of humic acids of the Ulaan-Ovoo coal is 14.5 % and the solubility in water is 23.20 %. The yield of humic acids and the water solubility of the Shivee-Ovoo coal are much higher than those of the Ulaan-Ovoo coal, because the coal of Shivee-Ovoo deposit is a highly oxidized brown coal, while the coal of the Ulaan-Ovoo deposit is a higher rank subbituminous coal. These results show that the humic acids of both kinds of coal have good penetration ability in soil and higher bioavailability for plants. The IR spectra of humic acids of both coals and their humic acids show that the organic matter of humic acids consists mainly of aliphatic and aromatic compounds with carboxylic (−COOH), carbonyl (>CO), hydroxyl (−OH) and etheric (−O−) groups, which are characteristic of highly oxidized organic matter. Humic acids of the Shivee-Ovoo coal exhibit a high biological activity in relation to Iren wheat seeds. The highest biological activity was detected for humic acid concentration of 0.005 %.

Keywords: the Shivee-Ovoo coal, the Ulaan-Ovoo coal, brown coal, humic acids, biological activity

INTRODUCTION

Humic acids (HAs) are oxygen-containing organic compounds; they are present in plants, peat and coal, mainly in oxidized brown coal.

Mongolia is one of the 10 coal-rich countries in the world with its 175 billion t of geologically estimated resources, including high-quality coking coal, bituminous stone coal, subbituminous middle-rank coal, and low-rank oxidized brown coal [1].

The Shivee-Ovoo and Ulaan-Ovoo coals are two of the most important kinds of brown coal. The estimated coal resources of the Shivee-Ovoo coal deposit account for 2.7 billion t, and the Ulaan-Ovoo coal deposit – for 174.5 million t. It is very important that both coal deposits are very close to the railway. The Shivee-Ovoo coal deposit is one of the largest in the Nyalga-Choir coal basin in the central economic region of Mongolia. The Shivee-Ovoo coal deposit is developed as an opencast mine since 1990, and coal from it is used for a long time at thermal power stations in Ulaanbaatar city. The Shivee-Ovoo coal deposit is located at the territory of Dalanjargalan village in the East Gobi province, at a distance of 300 km to the southeast of Ulaanbaatar, Mongolia [2].

The Ulaan-Ovoo coal deposit is one of the largest ones in the northern economic region of Mongolia and is located at the territory of Tushig village in the Selenge province, at a distance of 430 km to the north of Ulaanbaatar, Mongolia.

Usually, HAs in oxidized brown coals can be isolated by dissolving in the aqueous solutions of NaOH or KOH and obtaining as a black-brown coloured solid product after precipitation by HCl solution.

The studies aimed at characterization of humic acids isolated from brown coal of different deposits including the Baganuur and Shivee-Ovoo in Mongolia and development of the applications of humic compounds as fertilizers in agriculture and as preparations in veterinary medicine have been carried out for a long time by Sh. Munkhjargal [3] and J. Dugarjav [4].

Coal from the Ulaan-Ovoo deposit has not been studied thoroughly yet. Coal was analyzed and its HAs were isolated for the first time by us.

The purpose of the present work was to isolate HAs from the Shivee-Ovoo and Ulaan-Ovoo coals, determine the major technical properties, elemental composition, and biological activity, and investigate isolated HAs and the initial coal samples by means of IR spectroscopy and ^{13}C NMR spectroscopy.

EXPERIMENTAL

The analytical coal samples from the Shivee-Ovoo and Ulaan-Ovoo deposits were prepared for analysis according to ASTM D 2797. The main technical characteristics were determined by means of proximate and ultimate analysis according to the Mongolian National Standards MNS 656-79 (moisture content), MNS 652-79 (ash yield), MNS 654-79 (volatile matter yield), MNS 669-87 (gross calorific value) and MNS 895-79 (sulphur content).

Method for the determination of the humic acids yield

Portions (1 g) of the samples from the Shivee-Ovoo and Ulaan-Ovoo coal deposits were placed in conical flasks 250 mL in volume, and 50 mL of 5 % HCl solution was added. To provide extraction, this mixture in the conical flask was kept in a water bath at 50 °C for 2 h. Under these conditions, all HAs in the organic mass of coal were converted to free HAs. After cooling the mixture to room temperature, the liquid phase was removed by centrifuging at 2000 r.p.m. for 15 min. The centrifuged solid phase was dissolved in 100 mL of 1 % NaOH solution until a colourless solution was formed, and then 100 mL of 15 % HCl solution was added to the solution of HAs in 100 mL of 1 % NaOH solution. The mixture was kept for 24 h at room temperature until the HAs were completely precipitated. The HAs precipitate was separated by filtering through a paper filter, washed with distilled water, dried in an oven at 80–85 °C, and weighed to determine the yield of HAs in per cent.

Determination of water solubility of humic acids

To carry out extraction, 1 g of HAs (of coal samples from the Shivee-Ovoo or Ulaan-Ovoo deposits) and 100 mL of distilled water in a conical flask 250 mL in volume were placed in a water bath at 80 °C for 2h. After cooling, the mixture was centrifuged (2000 r.p.m.) for 15 min. The solid residue was washed again 2 times with 100 mL of distilled water and centrifuged once more. All the solutions formed from distilled water were separated from the solid residue by filtration through a paper filter; washing with distilled water was performed until colourless filtered solution was obtained. The solid residue after washing on filter paper was dried in an oven at 80 °C to achieve constant mass (the difference of the two sequential masses of dried samples should not exceed 0.001 g). The solubility (%) of HAs in water was calculated.

Method for the determination of the content of hematimilanic acids in humic acids

Portions (1 g) of humic acid sample was packed in filtering paper and extracted with ethanol in the Soxhlet apparatus until the extracting agent became colourless. After extraction, the solution in ethanol was placed in a vacuum evaporator to remove ethanol, and then dried at room temperature till the constant mass of the sample package. After that, the content of hematimilanic acids in HAs was determined (in per cent) by weighing.

The samples were investigated by means of the Fourier transform infrared (FTIR) spectroscopy with an Interspec 200-X series of FTIR spectrometers (Spectronic Camspec Ltd, Great Britain) with PIKE Diffusion IR accessories using a KBr disc containing finely ground samples (1 %). All the spectra were measured in the frequency range of 4000 to 400 cm^{-1}, and 32 scans were taken per sample.

The high-resolution ^{13}C NMR spectra of the HAs samples were recorded with an AVANCE III 300 WB (Bruker, Germany) instrument at a frequency of 75 MHz using a standard cross-polarization and magic angle spinning (CPMAS) procedure. Based on the results obtained by means of ^{13}C NMR spectroscopy, we calculated the structural group parameters of the HAs samples using the following formulas [5–8]:

1) the degree of aromaticity

$$f_a = C_{Ar-O} + C_{Ar}$$

2) the hydrophilic-hydrophobic parameter

$$f_{h/h} = (C{=}O + COOH + C_{Ar-O} + C_{O-Alk-O} + C_{Alk-O})/(C_{Ar} + C_{Alk})$$

3) the aromaticity/aliphaticity factor

$$f_{a/al} = (C_{Ar-O} + C_{Ar})/(C_{O-Alk-O} + C_{Alk-O} + C_{Alk})$$

The biological activity of HA samples was evaluated according to GOST (State Standard) 12038–84 and the published procedures [8–11]. The magnitude of the biological activity was expressed using the phytoactivity index (PI), which takes into account seed germination energy (GE), root length (RL), and sprout height (SH). The value of PI is a generalized index calculated as the average value of the sum of GE, RL, and SH values expressed in the fractions of a unit:

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

where GE, DK, and SH are the average values for three trays (% on a control basis).

The humic acids were tested as solutions (HumNa) with two concentrations: 0.0005 and 0.005 %. The range of concentrations was chosen due to the inhibitory effects of higher concentrations and the low efficiency of lower concentrations of HAs in solution. Seeds were germinated in special germinator trays between the layers of moistened filter paper. The HAs samples were tested in nine trays with 50 seeds: three trays were treated with a 0.0005 % solution of HAs, three trays were treated with a 0.005 % solution of HAs, and three trays were treated with distilled water (a control experiment). The values of GE, SH, and RL were measured on the fifth day. Seeds were germinated at a constant temperature of 20 °C without access to light. Wheat variety Iren was used.

RESULTS AND DISCUSSION

The results of proximate and ultimate analysis of coal samples from the Shivee-Ovoo and Ulaan-Ovoo deposits are shown in Table 1.

One can see that the content of volatile matter, the H/C ratio, carbon and oxygen content in the samples of both coal kinds are similar and indicate that coal samples from the Shivee-Ovoo and Ulaan-Ovoo deposits are highly oxidized low-rank coals because oxygen content is rather high in both coals. The total sulphur content is not high and, therefore, not dangerous for the environment.

The humic acids were isolated from the coal samples from the Shivee-Ovoo and Ulaan-Ovoo deposits; proximate and ultimate analyses of isolated HAs were carried out (Table 2). These results show that the ash content is increased almost by a factor of 2, the yield of volatile matter and oxygen content are increased too, while carbon content is

TABLE 1

The results of proximate and ultimate analyses of the Shivee-Ovoo and Ulaan-Ovoo coals

Coal deposit	Proximate analysis, %				Ultimate analysis, mass %				
	Moisture, W^a	Ash, A^d	Yield of volatile matter, V^{daf}	Caloric value, Q^{daf}, kcal/kg	Carbon, C^{daf}	Hydrogen, H^{daf}	Sulphur total, S_t	Oxygen and others, $(N + O)^{daf}$	H/C atomic ratio
Shivee-Ovoo	13.4	21.2	42.6	5961.2	71.3	5.0	1.1	22.6	0.94
Ulaan-Ovoo	6.0	4.9	44.8	6004.0	66.9	4.9	0.8	27.4	0.88

TABLE 2

Results of proximate and ultimate analyses of isolated humic acids from the coal of the Shivee-Ovoo and Ulaan-Ovoo deposits

Coal deposit	Yield of humic acids, %	Technical characteristics, %			Elemental composition, %			
		Moisture, W^a	Ash, A^d	Yield of volatile matter, V^{daf}	C^{daf}	H^{daf}	$(N + O)^{daf}$	Sulphur total, S_t^d
Shivee-Ovoo	23.2	9.3	42.3	55.7	57.3	3.5	38.7	0.5
Ulaan-Ovoo	14.5	3.8	7.6	49.5	55.9	4,0	39.6	0.5

TABLE 3

The yield of hematimilanic acid from humic acids of the Shivee-Ovoo and Ulaan-Ovoo coals

Coal deposit	Yield of, %	
	hematimilanic acid	hard residue (humus)
Shivee-Ovoo	43.0	57.0
Ulaan-Ovoo	22.1	77.9

TABLE 4

The yield of the water-soluble fraction in humic acids of the Shivee-Ovoo and Ulaan-Ovoo coals

Coal deposit	The yield of, %	
	water-insoluble solid residue	water-soluble fraction
Shivee-Ovoo	21.9	78.1
Ulaan-Ovoo	76.8	23.2

TABLE 5

Integral intensities of spectral regions according to the data of ^{13}C NMR (CPMAS) spectra of humic acids from the Shivee-Ovoo coal, %

Chemical shift, ppm							Structural parameter		
220–187	187–165	165–145	145–108	108–90	90–48	48–5			
C=O	COOH	C_{ar-O}	C_{ar}	$C_{O-alk-O}$	C_{alk-O}	C_{alk}	f_a	$f_{h/h}$	$f_{a/al}$
11.1	8.8	7.5	29.5	5.0	16.3	21.8	37.0	0.9	0.9

decreased in comparison with the data shown in Table 1. Usually, most of brown coals have 10–30 % HAs, and the yield of HAs from the Shivee-Ovoo coal is 23.2 %, which is a comparatively high yield. This value confirms that the Shivee-Ovoo coal is brown coal of B2 mark of lignite type with a high degree of oxidation.

The humic acids of the Shivee-Ovoo and Ulaan-Ovoo coals were dissolved in ethanol, and the yield of the ethanol-soluble fraction was determined. This is a so-called yield of hematimilanic acid from HAs of both coal kinds (Table 3). Also, HAs of the Shivee-Ovoo and Ulaan-Ovoo coals were dissolved in distilled water, and the yield of water-soluble fraction in HAs was determined for both coals (Table 4).

The data in Table 3 and 4 show that the yield of the ethanol-soluble fraction (hematimilanic acid) and the yield of the water-soluble fraction from HAs of the Shivee-Ovoo coal are much higher than those of HAs from the Ulaan-Ovoo coal. These fractions are the most important biologically active components in HAs, and therefore HAs of the Shivee-Ovoo coal are biologically more active than HAs of the Ulaan-Ovoo coal.

Usually, HAs are used for a wide range of applications in agriculture as humic fertilizer. The higher is water solubility of HAs, the higher is their soil-penetration ability, and the higher is their bioavailability for plants.

Unfortunately, the macromolecular structure of HAs and the mechanism of their biological activity have not been determined completely yet.

In the IR spectra of the Shivee-Ovoo coal, there are several weak absorption bands for –CH aromatic group at 698, 752, 800 cm^{-1}, medium-intensity bands of aliphatic –CH; $-CH_2$ and $-CH_3$ groups at 1249 cm^{-1} and sharp higher-intensity bands at 2854–2923 cm^{-1}. There are also strong absorption bands of >C=O groups at 1600 cm^{-1}, weak bands of –O– groups at 1400 cm^{-1} and C–O– groups at 1000, 1050 cm^{-1}. Strong but not sharp bands related to –OH and –NH groups appear at 3400 cm^{-1}. Therefore, the organic mass of coal from the Shivee-Ovoo deposit consists mainly of aliphatic, aromatic and aromatic-aliphatic structures with above-mentioned functional groups inside.

The IR spectra of HAs from the Shivee-Ovoo and Ulaan-Ovoo coals show that there are intense adsorption bands with the highest intensity at 1600–1700 cm^{-1}, related to –COOH and >C=O groups, which are the most important characteristic for HAs. There are also adsorption bands with medium intensities at 1306 and 1037 cm^{-1}, related to –C–O– and –O– groups. There is a broad adsorption band with lower intensity at 3200–3600 cm^{-1}, related to –OH groups connected with aliphatic and aromatic fragments. Adsorption bands with the lowest intensity at 2881 cm^{-1} relate to aliphatic $-CH_3$, $-CH_2-$ and >CH– groups, and the band at 800 cm^{-1} relates to –CH groups of aromatic ring structures. The IR spectra of HAs of the Shivee-Ovoo and Ulaan-Ovoo coals show that the organic matter of HAs consists mainly of aliphatic and aromatic compounds with carboxylic (–COOH), carbonyl (>CO), hydroxyl (–OH) and etheric (–O–) groups, which are characteristic of highly oxidized organic matter of the HAs.

The integral values of spectral regions in the ^{13}C NMR (CPMAS) spectra of HAs of the Shivee-

TABLE 6

Test functions and the integral index of phytoactivity of HumNa

HumNa concentration, %	Root length, cm*	Sprout height, cm*	Germination energy, %	Index of phytoactivity
0.0005	8.7 (−6.1)	6.0 (−6.8)	93.9	0.96
0.005	9.9 (+6.4)	8.0 (+24.1)	15.0	1.15

* The increments of a characteristic in comparison with control values (%) are given in parentheses.

Ovoo coal are shown in Table 5. The obtained values are typical for brown coals.

Table 6 summarizes experimental data on the determination of the biological activity of HumNa the Shivee-Ovoo coal by phytotesting, in the course of which not only the stimulation of the development of plants but also the suppression of certain test functions were established.

The concentration of humic preparations used is a factor affecting biological activity. The concentration of HAs from the Shivee-Ovoo coal equal to 0.005 % showed the highest values of PI (see Table 6).

CONCLUSIONS

1. Results of proximate and ultimate analysis of the Shivee-Ovoo and Ulaan-Ovoo coals confirmed that the Shivee-Ovoo coal is low-rank lignite coal of B2 mark, and the Ulaan-Ovoo coal is subbituminous coal. Both coal kinds are suitable raw materials for obtaining HAs.

2. Humic acids from the Shivee-Ovoo coal have been isolated in a higher yield.

3. The solubility of HAs of the Shivee-Ovoo and Ulaan-Ovoo coals in ethanol and water has been determined; the yield of the ethanol-soluble fraction (hematimilanic acid) and the yield of the water-soluble fraction are comparatively high, and these fractions are the most important biologically active components in HAs with higher penetration ability in soil and higher bioavailability for plants.

4. The IR spectra of HAs from the Shivee-Ovoo and Ulaan-Ovoo coals show that the HAs organic matter consists mainly of aliphatic and aromatic compounds with carboxylic (−COOH), carbonyl (>CO), hydroxyl (−OH) and etheric (−O−) groups, which are characteristic of the highly oxidized organic matter. The integral values of spectral regions in the ^{13}C NMR (CPMAS) spectra of HAs from the Shivee-Ovoo coal are typical for brown coals.

5. It was established in the experiments with wheat seeds that the index of phytoactivity of HAs extracted from the Shivee-Ovoo coal is higher in comparison with the reference test. The largest effect is for humate concentration equal to 0.005 % (PI = 1.15).

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