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INVESTIGATION ON HUMIC ACIDS OF SHIVEE-OVOO COAL

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The coal of Shivee-Ovoo deposit was analyzed by proximate and ultimate analysis and have been confirmed that the Shivee-Ovoo coal is a low-rank lignite coal of B2 mark and it is suitable raw material for humic acids. A humic acids with higher yield — 23,22% have been isolated from the Shivee-Ovoo coal. The solubility of humic acids of Shivee-Ovoo coal in ethanol — 43,0% and water — 78,5% was determined and the yield of ethanol soluble fraction (hematimilanic acid) and the yield of water soluble fraction are comparatively higher and these fractions are most important biologically active components in the humic acids with higher penetration ability in soil higher bioawilability by plants. The IR spectra of humic acids of Shivee-Ovoo coal and it's humic acids show that the organic matter of humic acids consists mainly aliphatic and aromatic compounds with carboxylic (-COOH), carbonyl (>CO), hydroxyl (-OH) and etheric (-O-) groups which are characteristics of highly oxidized organic matter.
Keywords: Shivee-Ovoo coal, pyrolysis, brown coal, humic acid, lignin, biologically active components, IR spectra, organic substances of humic acids.

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Humicacids (humicsubstances) are oxygen containing organic compounds and contain in the plants, peats and coals mainly oxidized brown coals.

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

The Shivee-Ovoo coal is one of the most important lignite brown coal of B2 mark withit's estimated coal resources is 2,7 billion tones and Shivee-Ovoo coal deposit is very near to the railway. The Shivee-Ovoo brown 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 working as an open-cast mine since 1990 and is using for long time in thermal power stations in Ulaanbaatar city. The Shivee-Ovoo coal deposit is located in the territory of the village "Dalanjargalan" of the East-Gobi province 300 km southeast of Ulaanbaatar, Mongolia [2].

Usually humic acids in oxidized brown coals can be isolated by dissolving in NaOH or KOH water solutions and to obtain as a black-brown colored hard product after precipitation by HCl solution.

Our doctors Sh. Munkhjargal [3] and J. Dugarjav [4] have worked for long time on investigation of characterization and properties of humic acids isolated from brown coals of different deposits in Mongolia and applications of humic fertilizers in agriculture and preparates in veterinary in Mongolia.

The purpose of present work was isolation of humic acids from Shivee-Ovoo coal and to determine main technical properties, elemental composition and investigation by IR analysis of the isolated humic acids and initial coal sample.

Experimental

The analytical coal samples of Shivee-Ovoo deposit were prepared for analysis according to ASTM D 2797. The main technical characteristics such as proximate and ultimate analysis were performed according to 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 determination of the yield of humic acids: 1gr sample of Shivee-Ovoo coal placed in conic flask of 250 ml and added 50 ml 5% solution of HCl. This mixture in conic flask put in a water bath at 50^{o}C for 2 h extraction. At this condition all humic acids in coal organic mass converted to free humic acids. After cooling the mixture until room temperature the liquid phase removed by centrifugation at 2000 rotation/min. for 15 min. The centrifuged solid phase was washed (dissolved) with 100 ml 1% solution of NaOH until colorless of washed solution and the liquid phase obtained by centrifugation at 2000 rotation/min. for 15 min. Was added 100 ml 15% solution of HCl to the solution of humic acids in 100 ml 1% solution of NaOH and kept 24 h in room temperature until completely precipitation of humic acids. The humic acids precipitation obtained by filtering on a filter paper and washed with distilled water and

then dried in a oven at 80-85°C and weighed for determination of the yield humic acids in %.

Determination of water solubility of humic acids: 1 g humic acids of Shivee-Ovoo coal and 100 ml distilled water in 250 ml of conic flask put in a water bath at 80°C for 2 h extraction. After cooling the mixture was centrifuged (2000 rotation/min) for 15 min. The solid residue was washed again 2 times with 100 ml distilled water and centrifuged again. All solutions of distilled water removed from the solid residue by filtration on a filter paper and washed with distilled water until colorless of filtered solution. The washed solid residue on filter paper was dried in oven at 80°C until constant weigh (the difference of the weights of dried samples between two weighing should not exceed 0,001 g) and calculated the water solublity of humic acids in %.

Method for determination of content of hematimilanic acids in humic acids: 1 g of humic acid sample packed by filtering paper and extracted by ethanol in Sokxlet apparatus until colorless extracting agent of ethanol. After extracting the solution in ethanol put in vacuum evaporator for removing the ethanol and dried in room temperature until the constant weight of package of the sample and then determined the content of hematimilanic acids in humic acids by weighing in %.

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

Results and discussion

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

The results of proximate and ultimate analysis in Table 1 for example the content of volatile matter, the ratio of H/C=0.84, carbon and oxygen content indicate that coal from Shivee-Ovoo deposit is a low rank B2 (ISO 11760) brown coal. The content of total sulfure is not higher and not so dangerous for the environment.

Table 1

Proximate and ultimate analyses of Shivee-Ovoo coal

Sample	Proximate analysis, %				Ultimate analysis, %			
	Moisture, W^a	Ash, A^d	Volatile matter, V^{daf}	Caloric value, Q^{daf}, kcal/kg	Carbon, C^{daf}	Hydro-gen, H^{daf}	Sulfure total, St	Oxygen and others, $(N+O)^{daf}$
Shivee-Ovoo coal	13,41	21,17	42,57	5961,2	71,35	4,99	1,06	22,60

Have been isolated the humic acids from the Shivee-Ovoo coal and determined the results of proximate and ultimate analysis of humic acids from the coal Shivee-Ovoo deposit (Table 2).

Table 2

Results of proximate and ultimate analysis of humic acids from the coal Shivee-Ovoo

Yield of humic acids, %	Technical characteristics				Elemental compostion			
	W^a, %	A^d, %	V^a, %	V^{daf}, %	C^{daf}, %	H^{daf},%	S^a, %	$(N+O)^{daf}$, %
23.22	9.32	42.32	29.12	55.67	57.30	3.50	0.5	38.7

The results of proximate and ultimate analysis of humic acids from the coal Shivee-Ovoo deposit in Table 2 show that the ash content increased almost 2 times, also increased intensively the yield of volatile matter and oxygen content and decreased only the carbon content in comparison with the dates in Table 1. Usually most of brown coals have 10-30% humic acids and the yield of humic acids in Shivee-Ovoo coal is 23,22%, which is a comparatively higher yield and confirms that the Shivee-Ovoo coal is a brown coal of B2 mark of lignite type with higher degree of oxidation.

Table 3

The yield of hematimilanic acid in humiccaids of Shivee-Ovoo coal

Sample	Yield of hematimilanic acid, %	Hard residue orhumus, %
Humic acids of Shivee-Ovoo coal	43.0	57.0

The humic acids of Shivee-Ovoo coal was dissolved in ethanol and determined the yield of ethanol soluble fraction, which equal to so called the yield of hematimilanic acid in humiccaids of Shivee-Ovoo coal (Table 3). Also the humic acids of Shivee-Ovoo coal was dissolved in distillede water and determined the yield of water soluble fraction in humic acids of Shivee-Ovoo coal (Table 4).

Table 4

The yield of water soluble fraction in humiccaids of Shivee-Ovoo coal

Sample	Hard residue, %	The yield of water soluble fraction, %
Humic acids of Shivee-Ovoo coal	21.95	78.05

The dates in Table 3 and 4 show that the yield of ethanol soluble fraction (hematimilanic acid) and the yield of water soluble fraction are comparatively higher and these fractions are most important biologically active components in the humic acids.

Usually humic acids are using wide range of applications in agriculture as humic fertilizer for many years. When the water solubility of humic acids is higher than the penetration ability of them in soil, then is higher and the bioavailability by plants is also.

Unfortunately the macromolecular structure ofhumic acids and mechanism of the biological activity are not determined completely.

As shown in Table 4, the sulfuric acid (78.05%) in the Shivee-Ovoo sediment dissolves, indicating that it is well tolerated in the soil and may be useful for plant growth due to its high incubation.

To characterize the organic matter of the Shivee-Ovoo coal has been analyzed by IR analysis and the IR spectra is shown in Fig. 1.

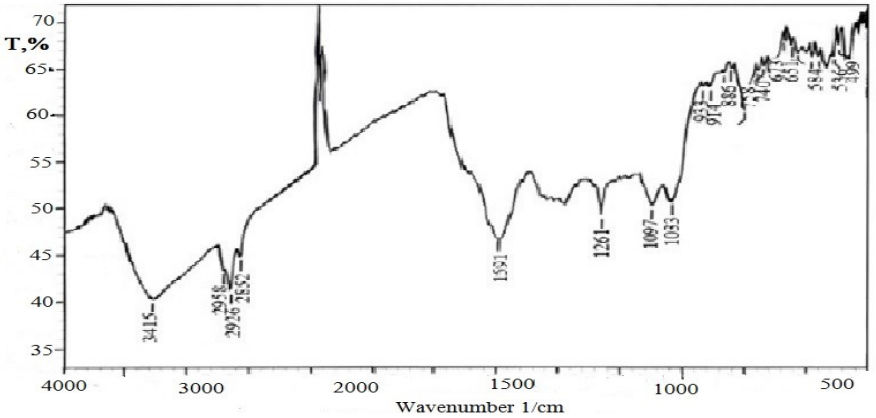

Fig. 1. The IR spectra of coal from Shivee-Ovoo deposit

In the IR spectra (Fig. 1) of Shivee-Ovoo coal there are severalweek absorption bands for -CH aromatic group at 698, 752, 800 cm^{-1} and for aliphatic -CH; $-CH_2$ and $-CH_3$ groups with middle intensity at 1249 cm^{-1} and a sharp bands with higher intensity at 2854-2923 cm^{-1}. And and also a strong absorption bands for >C=O groups at 1600 cm^{-1}, week bands for -O- groups at 1400 cm^{-1} and for C-O- groups at 1000, 1050 cm^{-1}. A unsharp and strong band for -OH and -NH groups at 3400 cm^{-1}. Therefore the coal organic mass of Shivee-Ovoo coal consist mainly aliphatic, aromatic and aromatic-aliphatic structures with above mentioned functional groups inside.

Also the isolated humic acids of Shivee-Ovoo coal have been analyzed by IR analysis and the IR spectra is shown in Fig. 2.

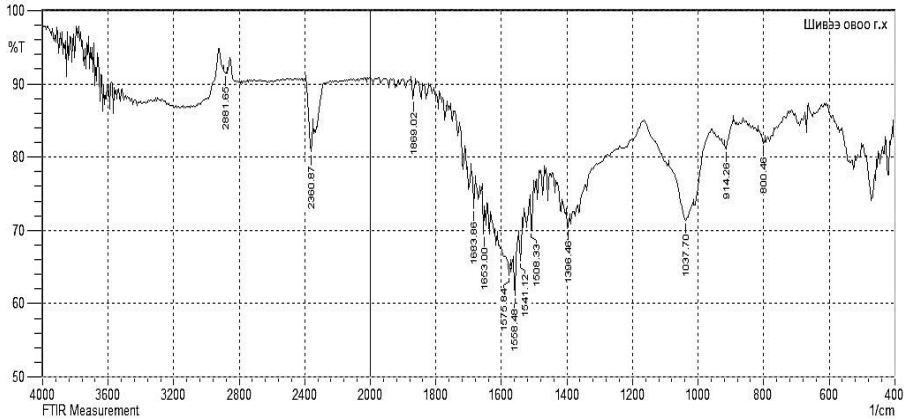

Fig. 2. The IR spectra of humic acids of Shivee-Ovoo coal

The IR spectra of humiccaids of Shivee-Ovoo coal show that there is a big adsorption bands with highest intensity at 1508-1683 cm^{-1} for –COOH and >CO groups which are the most important characteristic for humic acids. Also there are adsorption bands with middle intensities at 1306 and 1037 cm^{-1} for –C-O- and –O- groups. There is a unsharp wide adsorption band with lower intensity at 3200-3600 cm^{-1} for –OH groups connected with aliphatic and aromatic fragments. A adsorption bands with lowest intensity at 2881 cm^{-1} for aliphatic $–CH_3$; $-CH_2-$ and >CH- groups and at 800 cm^{-1} for –CH groups of aromatic ring structures. The IR spectra of humic acids of Shivee-Ovoo coal show that the organic matter of humic acids consists mainly aliphatic and aromatic compounds with carboxylic (-COOH), carbonyl (>CO), hydroxyl (-OH) and etheric (-O-) groups which are characteristics of highly oxidized organic matter of the humic acids.

Conclusions

1. On the basis of proximate and ultimate analysis of Shivee-Ovoo coal have been confirmed that the Shivee-Ovoo coal is a low-rank lignite coal of B2 mark and it is suitable raw material for humic acids.
2. A humic acids with higher yield — 23,22% have been isolated from the Shivee-Ovoo coal.
3. The solubility of humic acids of Shivee-Ovoo coal in ethanol — 43,0% and water — 78,5% was determined and the yield of ethanol soluble fraction (hematimilanic acid) and the yield of water soluble fraction are comparatively higher and these fractions are most important biologically active components in the humic acids with higher penetration ability in soil higher bioavailability by plants.
4. The IR spectra of humic acids of Shivee-Ovoo coal show that the organic matter of humic acids consists mainly aliphatic and aromatic compounds with carboxylic (-COOH), carbonyl (>CO), hydroxyl (-OH) and etheric (-O-) groups which are characteristics of highly oxidized organic matter.
5. The IR spectra of humic acids of Shivee-Ovoo coal show that the organic matter of humic acids consists mainly aliphatic and aromatic compounds with carboxylic (-COOH), carbonyl (>CO), hydroxyl (-OH) and etheric (-O-) groups which are characteristics of highly oxidized organic matter of the humic acids.

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ИССЛЕДОВАНИЕ ГУМИНОВЫХ КИСЛОТ ИЗ УГЛЯ МЕСТОРОЖДЕНИЯ ШИВЭЭ-ОВОО

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Уголь месторождения Шивээ-Овоо был проанализирован с помощью прямого и окончательного анализов, вследствие чего было подтверждено, что уголь Шивээ-Овоо является низкосортным лигнитовым углем марки В2 и является подходящим сырьем для гуминовых кислот. Из угля Шивээ-Овоо были выделены гуминовые кислоты с наиболее высоким выходом (23,22%). Была определена растворимость гуминовых кислот угля Шивээ-Овоо в этаноле-43,0% и воде (78,5%), а выход растворимой в этаноле фракции (гиматомелановая кислота) и выход растворимой в воде фракции оказались сравнительно высокими, а именно эти фракции являются наиболее важными биологически активными компонентами в гуминовых кислотах, с более высокой проникающей способностью в почве и более высокой биологической доступностью для растений. ИК-спектры гуминовых кислот угля Шивээ-Овоо и его гуминовых кислот показали, что органическое вещество гуминовых кислот состоит в основном из алифатических и ароматических соединений с карбоновыми (-COOH), карбонильными (>CO), гидроксильными (-OH) и эфирными (-O-) группами, которые характеризуют сильно окисленные органические вещества.
Ключевые слова: Шивээ-овоо уголь, пиролиз бурого угля, гуминовые кислоты, лигнин, биологически активные компоненты, ИК-спектры, органические вещества гуминовых кислот.