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Spectral Studies of Humic and Fulvic Acids of Brown Coals

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Abstract

Results of investigation into the composition of humic acids (HA) and fulvic acids (FA) isolated from brown coals by means of proximate and ultimate analysis, IR, and EPR spectroscopy are presented. It is shown that the yield of HA exceeds the yield of FA. The maximum yield (60–68 %) was detected for HA from naturally oxidized brown coal. It has been established that lignite FA and HA have significant differences in the structural and group composition: FA are characterized by the higher content of the fragments of aliphatic structures, alcohols, carboxylic acids, and esters. Humic acids are characterized by the higher content of aromatic fragments.

Keywords: brown coal, humic acids, fulvic acids, IR spectroscopy, EPR spectroscopy

INTRODUCTION

Brown coal (BC) is a promising raw material for obtaining humic substances (HS), which are a complex mixture of natural high-molecular organic compounds. Due to specific properties, HS may be used efficiently in different branches of industry and agriculture. Especially valid characteristics of HS are their biological activity with respect to plants [1–3]. Humic substances are composed of several fractions. According to the classification based on the solubility of HS components in alkalis, acids and alcohols, humic acids (HA) form a fraction soluble in alkalis and insoluble in acids (pH < 2); fulvic acids (FA) comprise a fraction of HS which is soluble in alkalis and in acids, and remains in filtrate solution after HA precipitate is formed and separated; hymatomelanic acids are HA components soluble in ethanol [4, 5]. The high solubility of FA is due to lower molecular mass in comparison with HA and higher oxidation degree [6]. There are several points of view on the nature of FA formation. One of them is based on the hypothesis that FA are self-consistent chemical compounds [7, 8]. According to another hypothesis, FA are initial forms or products of HA destruction [9, 10]. An assumption has also been formulated that there is binding between the groups of FA and HA in the humus of soil and peat in the form of complicated ester complexes that are stable against the action of acids and saponifiable under the action of alkalis.

By present, FA for soils of various geneses, peat, sediments and natural waters have been described rather extensively. Statistically averaged elemental composition of FA, %, is: C 40–50, O 44–52, H 4–7, N 0.5–4, S 0–2. The number of functional groups is: carboxylic groups 500–1200 mg-equiv/100 g, phenol hydroxyls 30–600 mg-equiv/100 g. The data of IR and NMR spectroscopy confirm the presence of aliphatic, aromatic and carbohydrate fragments in FA [11]. Aromatic fragments comprise a smaller por-

tion of the chemical composition of FA in comparison with HA [12].

The functional group composition of FA varies within a rather broad range and depends on the isolation procedure. It has been established that FA of humus, obtained according to Forsyth's method, differ from the acids obtained according to Tyurin's method by decreased carbon content, increased oxygen content, and are characterized by higher molecular homogeneity at smaller molecular mass [13].

The most representative HS fraction isolated from brown coal is HA fraction. Its composition and properties have been studied rather thoroughly. Most frequently, the sources of FA as the subject of investigation are soil and peat. Much lower number of studies deal with the composition and properties of FA isolated from brown coal. Currently applied isolation procedures, composition and properties of FA extracted from soil and peat cannot be projected in full to FA from brown coal. At the same time, development of integrated processing of brown coal for the purpose of obtaining valuable products of coal chemistry (bitumen, HA) actualizes the development of industrially applicable procedures for FA extraction from the waste – an acid filtrate after obtaining powdered HA. Along with this, investigation of the functional-group composition and properties of FA from brown coal will accelerate their introduction as efficient biologically active additives in cattle breeding [14, 15], as plant growth stimulators [16], preparations for wastewater and soil purification from heavy metals [17]. These studies will promote the search for new promising directions in the use of FA in various branches of industry, taking into account the features of chemical and structural-group composition.

The goal of the present work is a comparative investigation of the elemental and structural-group composition of HA and FA extracted from BC.

EXPERIMENTAL

Materials

Humic and fulvic acids extracted from brown coal of the Tisul deposit at the Kans-Achinsk basin (BCTS), its naturally oxidized form (BSTSO) and brown coal samples from different regions of the Tyulgan deposit at the South Ural basin (BCT 30 and BCT 31) are chosen for investigation.

Procedures

Humic acids were extracted from a 1 g portion of coal using a 1 % aqueous solution of NaOH or KOH (100 mL) by heating up to 98 °C for 2 h. Thus obtained solutions of sodium humate (HumNa) or potassium humate (HumK) were acidified with HCl to pH 1–2, precipitated HA were separated by filtering, washed with distilled water to the neutral pH in washing water, and dried. Fulvic acids were obtained according to the scheme shown in Fig. 1 [18]. The filtrate obtained after HA precipitation, containing FA, was transferred into a glass flask 1000 mL in volume, and *n*-butanol was added in the amount of 100 mL. This solution under permanent mixing was heated in a water bath to 70 °C for 30 min. Then the solution was transferred into the separating funnel, where it was stirred for 15 min to achieve layering into the aqueous and organic (*n*-butanol) fractions. The major part of FA from the aqueous acid fraction was extracted into the butanol fraction. For a more complete extraction, the aqueous fraction was poured into a separate flask, into which 100 mL of *n*-butanol was added, and then FA extraction was repeated. Process completeness was concluded when the refractive index (r.i.) of the aqueous fraction was constant at $n = 1.343$ at 20 °C (for *n*-butanol, $n = 1.399$). Refractive index was measured with an IRF-454 refractometer (Russia). The organic fraction containing FA was washed in the separating funnel with distilled water to remove excess HCl till the neutral pH of washing water was achieved, and then transferred into the rotary film evaporator to remove *n*-butanol. Thus concentrated FA were then dried to constant weight in the vacuum drying box for 12 h at a temperature of 85–87 °C (medium vacuum, 3.0 Pa).

Investigation methods

IR spectra were recorded in dry KBr using an INFRALYUM FT-801 IR Fourier spectrophotometer (Russia) with the resolution of 4 cm^{-1} accumulating 64 scans within the range of 4000–500 cm^{-1}. The ratio KBr/образец = 200 : 1. Spectra were interpreted according to [19, 20].

Electron paramagnetic resonance (EPR) spectra were recorded with a Bruker EMX Micro 6/1 EPR

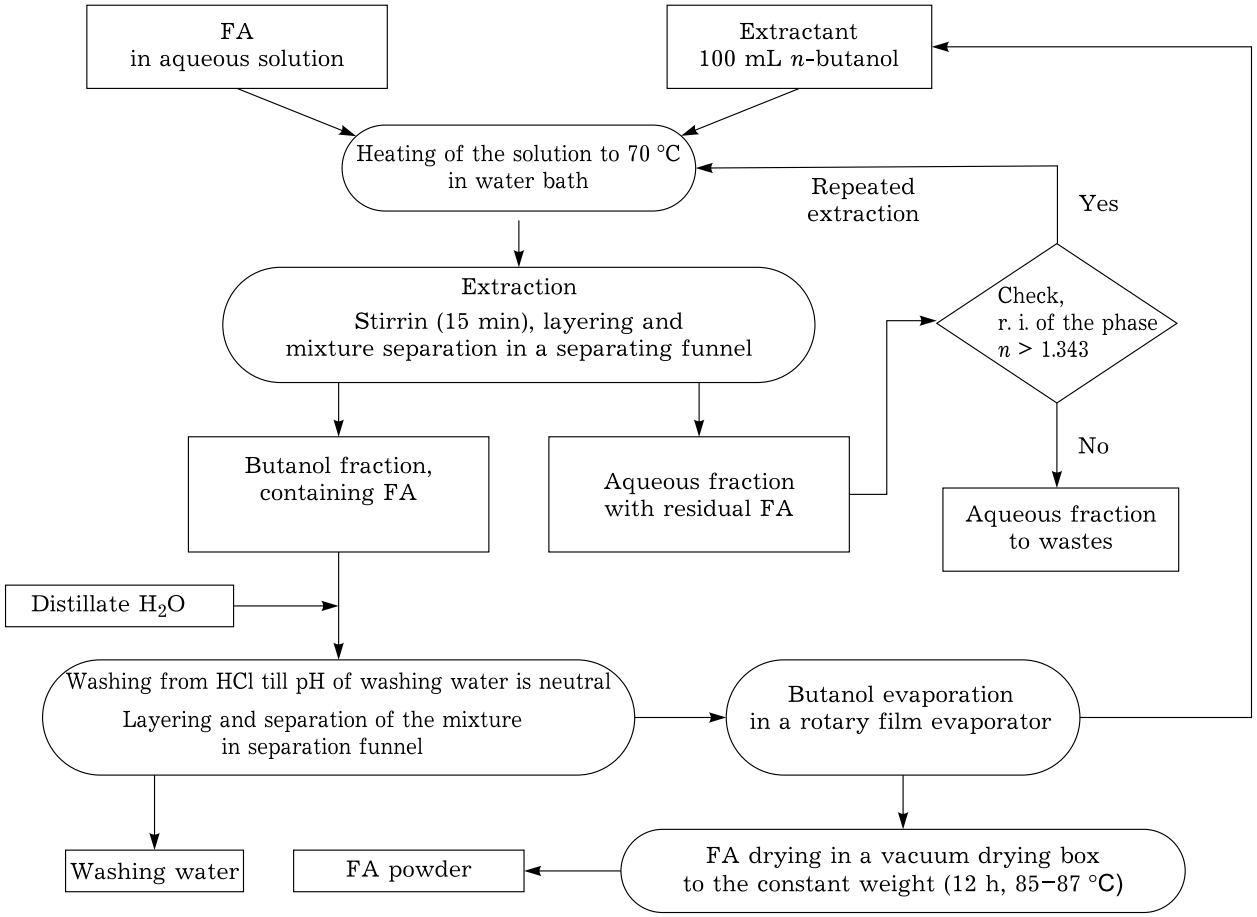

Fig. 1. Flowchart of the extraction of fulvic acids (FA) from the aqueous solution (r. i. is refractive index).

spectrometer (Germany). Calculation of the number of paramagnetic centres (PMC) was carried out by comparing with the standard sample (Mn^{2+} ions in MgO). The frequency of microwave radiation was about 9.8 GHz, with the SHF generator power of 1.8 mW; modulation frequency was 100 kHz with the amplitude of 1 G. Spectra were recorded accumulating 5 scans to improve the signal to noise ratio. The recorded spectra were processed using WinEPR software package.

RESULTS AND DISCUSSION

The data of proximate and ultimate analysis of initial coal samples, humic and fulvic acids are presented in Table 1. Fulvic acids isolated from all coal samples differ from HA by the lower carbon content and higher content of oxygen, nitrogen and sulphur. The lowest HS yield is characteristic of brown coal from the Tisul deposit (BCTS): HA – 22–25 %, FA – ~0.1 %. The highest HS yield is characteristic of the same coal in the oxidized form (BCTSO): HA – 60–68 %, FA – 7–9 % per daf coal.

The distinguishing features of FA and HA of brown coal according to the data of proximate and ultimate analysis agree with the results of the investigation of standard samples of FA and HA from peat (Pahokee Peat) and soil (Elliott Soil), International Humic Society (IHSS). According to IHSS results, an increase in the total content of heteroatoms (O, N and S) in FA is provided mainly by the high oxygen content [21].

The IR absorption spectra of initial coal samples (Fig. 2–4), HA and FA isolated from sodium humate are characterized by the presence of an intense absorption bands within frequency range 3500–3400 cm^{-1} – stretching vibrations of hydrogen-bonded O–H groups; 2920–2960 and 2870 cm^{-1} – stretching vibrations of CH_3 and CH_2 groups; 1700–1740 cm^{-1} – stretching vibrations of C=O groups in acids; 1100–1040 cm^{-1} –C–O bonds in alcohols, ethers. Absorption within this region may also be attributed to the mineral components of the samples. The absorption band at

TABLE 1

Proximate and ultimate analysis of initial coal, humic (HA) and fulvic acids (FA), %

Sample	W^a	A^d	V^{daf}	C^{daf}	H^{daf}	$(O + N + S)^{daf}$	Yield, %
			BCTS				
Coal	8.3	10.3	48.3	61.4	5.1	33.5	–
HA HumNa	6.1	1.1	–	56.3	5.1	38.6	22.1
HA HumK	6.4	2.8	–	66.5	4.3	29.2	25.1
FA HumNa	1.48	12.35	–	43.2	6.03	50.82	~0.1
FA HumK	0.62	4.78	–	45.0	5.64	49.33	~0.1
			BCTSO				
Coal	10.0	43.5	–	69.3	6.0	24.7	–
HA HumNa	10.6	10.9	–	59.7	6.2	34.1	60.9
HA HumK	4.6	17.0	–	46.2	3.2	50.6	68.0
FA HumNa	1.85	6.56	–	40.6	5.22	54.1	9.6
FA HumK	1.12	13.12	–	41.1	6.95	52.0	7.4
			BCT 30				
Coal	21.5	26.7	71.5	66.7	8.5	24.8	–
HA HumNa	0.6	20.5	–	61.6	8.6	29.8	38.0
HA HumK	5.6	17.5	–	63.7	8.1	28.2	41.3
FA HumNa	1.4	3.4	–	48.0	4.8	47.2	2.3
FA HumK	2.3	1.9	–	40.0	5.3	54.7	4.6
			BCT 31				
Coal	9.1	21.5	64.4	63.7	5.9	30.4	–
HA HumNa	0.7	13.4	–	53.2	10.5	36.3	38.5
HA HumK	5.5	2.7	–	59.0	7.2	33.8	42.0
FA HumNa	1.3	4.0	–	50.0	5.4	44.6	4.4
FA HumK	2.6	4.0	–	52.0	6.8	41.2	2.2

Note. W^a – analytical moisture according to GOST R 52917-2008; A^d – ash content per dry sample according to GOST 11022-95; daf – dry ash-free state of the sample; V^{daf} – content of volatile substances according to GOST 6382-2001; C^{daf}, H^{daf} – element content according to GOST 2408.1-95; $(O + N + S)^{daf}$ – by difference, yield of free acids according to GOST 9517-94. Measurement error: not more than 2 %.

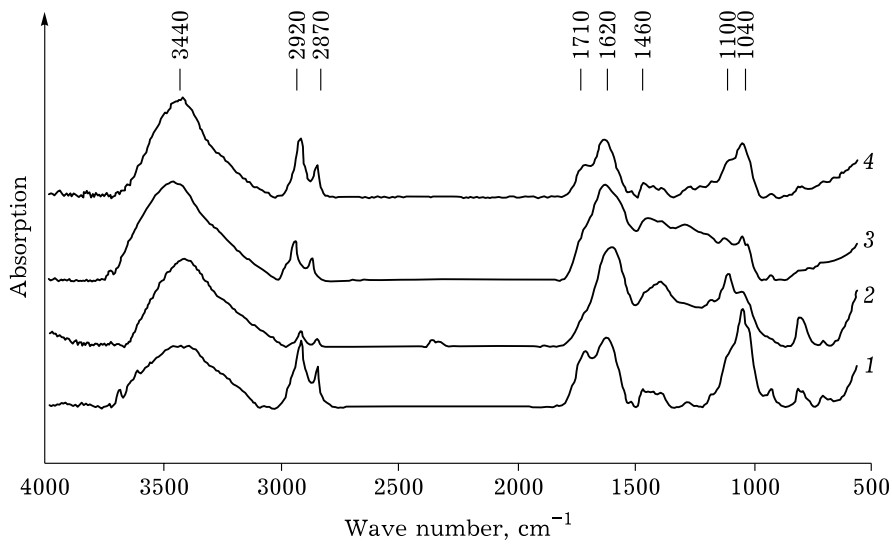

Fig. 2. IR spectra of brown coal samples: *1* – BCT 30; *2* – BCTSO; *3* – BCTS; *4* – BCT 31.

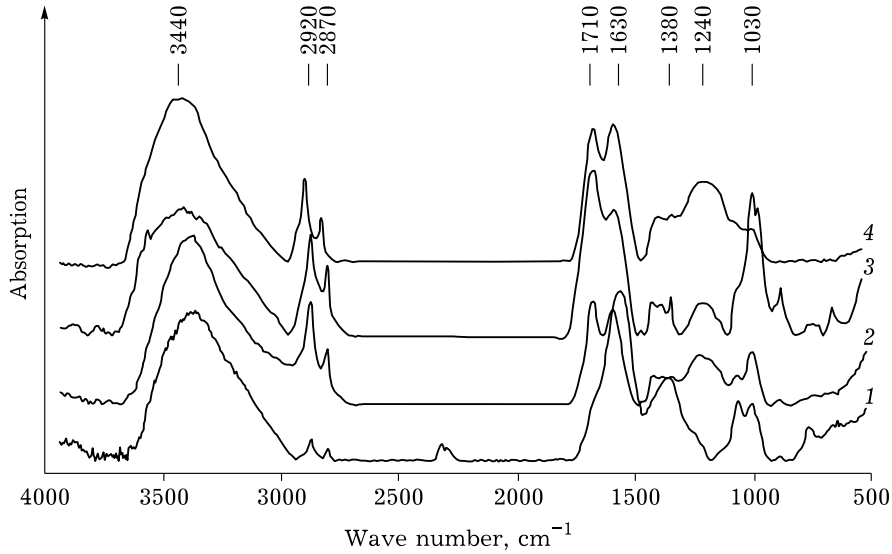

Fig. 3. IR spectra of HA HumNa: *1* – BCTSO; *2* – BCT 31; *3* – BCT 30; *4* – BCTS.

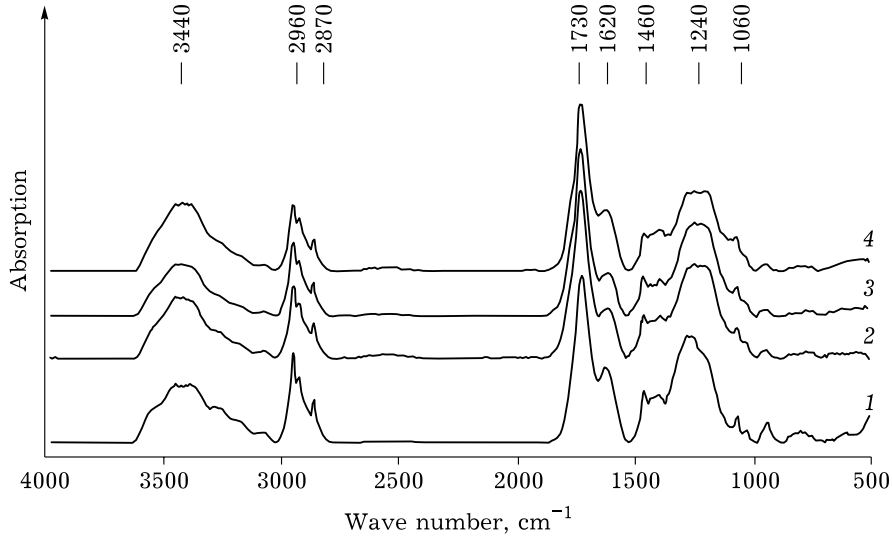

Fig. 4. IR spectra of FA HumNa: *1* – BCTSO; *2* – BCT 31; *3* – BCT 30; *4* – BCTS.

1620 cm^{-1} may be related to the vibrations of aromatic C=C bonds. The C=C bonds forming a linear conjugation system also may absorb within this region; the vibrations of carbonyl group C=C=O involved in conjugation system cannot be excluded, too. To decrease the effect of molecular water on the intensity of absorption bands within this region, the samples under investigation were dried preliminarily to the constant weight, and KBr was annealed. The presence of aromatic structures is revealed by the presence of an absorption band at 1460 cm^{-1}, which may be overlapped by the absorption band related to the bending vibrations of CH_2 group. Similar spectra were recorded for HA and FA isolated from HumK.

Unlike for the IR spectra of initial coal samples, the spectra of HA and FA are characterized by the presence of more intense bands at the frequency of 1710 cm^{-1} – stretching vibrations of C=O bonds in carboxylic acids, and 1240 cm^{-1} – stretching vibrations of C–O bands in carboxylic acids, esters and O–H bands in phenols (see Fig. 2–4). More intense bands in the spectra of FA at 2960 and 2870, 1730 and 1240 cm^{-1} provide evidence of the prevalence of aliphatic fragments, alcohols, ethers and carboxylic acids in FA structure.

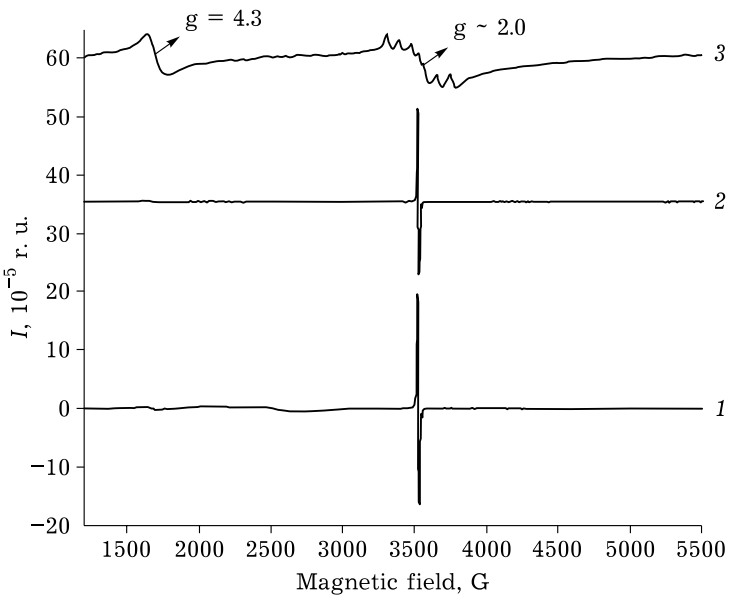

Fig. 5. EPR spectra of brown coal samples: BCTS (*1*); HA (*2*) and FA (*3*) obtained from sodium humate.

EPR spectra of BCTS coal samples, along with HA and FA extracted from them, are shown in Fig. 5 as example. The spectra of samples contain the signals from isolated Fe^{3+} ions with *g*-factor 4.3 [22, 23]. The signal from organic radicals with *g*-factor close to 2.0 is often observed against a background of a broad band, which is related to the presence of Fe^{3+} clusters bound through dipole-dipole interaction [23]. The EPR spectrum of a sample of demineralized coal is characterized by the absence both of signal asymmetry and of a signal with *g*-factor 4.3. So, Fe^{3+} ions that are present in the samples form only weak bonds with the organic matrix and are removed during demineralization. In addition to the signal from organic radicals, the EPR spectra of FA contain also six lines related to the superfine structure (SFS) of isolated Mn^{2+} ions (see Fig. 5). It is known [24, 25] that the average value of SFS constant (*A*) (that is, the average distance between the neighbouring lines of Mn^{2+} sextet, measured in Gauss units) depicts the ionicity degree of bonds participated by manganese and the organic matrix. For instance, in the case of the formation of ionic manganese complexes with such ligands as H_2O and F^-, the average SFS value is 98 G. With an increase in the fraction of bond covalence, the value of SFS constant decreases. The average value of SFS constant for all FA samples is the same and equals 88 G. A decrease in SFS constant in comparison with the value of $A(Mn^{2+})$ in the ionic state may be due to partial bonding between Mn^{2+} ions and the organic matrix [24, 25]. The fraction of Mn^{2+} ions bound with the organic matrix is about 10 %. Analysis of the mineral components of BCTS and BCTSO coal samples revealed the presence of manganese in the form of MnO, at a level of 0.17 and 0.14 % before HS extraction, 0.07 and 0.1 % after HS extraction, respectively. The highest intensity of the signal from Mn^{2+} (with respect to the radical signal) is observed in FA sample obtained from BCTS brown coal. The spectra of HA also contain low-intensity signals from Mn^{2+}. The signals of this type are absent from initial coal samples, or they are undistinguished due to their low intensity in comparison with the signals from radicals of organic nature. Attention is to be paid to the prevalence of the left shoulder of the signal at the magnetic field of 1000–2000 G in the EPR spectra of FA and HA (see Fig. 5), the presence of which is connected with superposition of the signal with *g*-factor equal to 5.0. This may be due to the presence of complexes with rhombic distortion of the octahedral complex typical for Mn^{2+} [25]. So, the samples contain Mn^{2+}–FA or Mn^{2+}–HA complexes with octahedral coordination, with rhombic distortions.

The major characteristics of EPR spectra of coal, humic acid and fulvic acid samples are presented in Table 2. One can see in Table 2 and in Fig. 6 that the concentration of paramagnetic centres (PMC) and the intensity of the radical signal decrease as a sequence: BC > HA > FA. For

TABLE 2

Main characteristics of the EPR spectra of coal samples, humic acids (HA) and fulvic acids (FA)

Sample	N, spin/g	g-factor	ΔH, G	$N(Mg^{2+})$, spin/g
BCTS	$1.19 \cdot 10^{17}$	2.0035	4.16	–
Demineralized BCTS	$6.31 \cdot 10^{16}$	2.0034	4.91	–
HA HumNa BCTS	$8.39 \cdot 10^{16}$	2.0034	5.14	–
FA HumNa BCTS	$6.31 \cdot 10^{13}$	2.0023	6.93	$4.10 \cdot 10^{14}$
BCT 30	$1.42 \cdot 10^{16}$	2.0034	4.16	–
HA HumNa BCT 30	$1.16 \cdot 10^{16}$	2.0034	6.24	–
FA HumNa BCT 30	$2.16 \cdot 10^{14}$	2.0023	6.04	$1.30 \cdot 10^{13}$
BCT 31	$3.04 \cdot 10^{16}$	2.0036	7.47	–
HA HumNa BCT 31	$1.70 \cdot 10^{16}$	2.0035	5.76	–
FA HumNa BCT 31	$3.80 \cdot 10^{15}$	2.0023	5.79	$2.22 \cdot 10^{13}$

FA samples, g-factor value coincides with g-factor of the free electron and differs substantially from g-factors of BC and HA. This fact is evidence in favour of the similar nature of radicals in BC and HA and their substantial differences from the radicals in FA. Close values of g-factor in BC (see Table 2) to 2.0036±0.0002 are evidences that the major role in paramagnetism of initial BC is played by polycyclic aroxyl radicals of semiquinone and phenoxyl nature [26]. However, the nature of radicals in HA obtained from corresponding coal samples does not undergo any changes, only their amount decreases regularly. Lower value of g-factor of FA in comparison with g-factor of BC and HA may be due to the presence of PMC of different nature in the structure of FA: aromatic radicals with larger amount of aliphatic fragments.

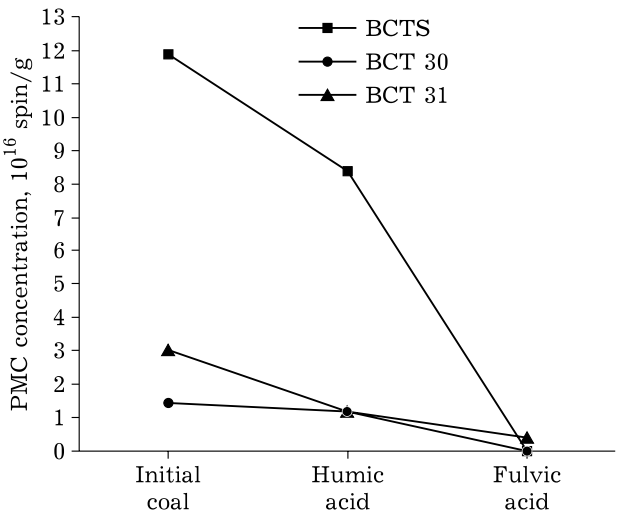

Fig. 6. Changes in the concentration of paramagnetic centres (PMC) in samples.

CONCLUSION

The proposed procedure allows achieving a high yield of valuable products, HA and FA, which is an essential factor for integrated BC processing. The highest HS yield is characteristic of the oxidized form of brown coal from the Tisul deposit (BCTSO): HA – 68.0 %, FA – 9.6 % per daf coal.

Results of proximate and ultimate analysis, IR spectroscopy demonstrate that HA are characterized by the higher content of carbon and aromatic fragments.

A distinguishing feature of FA is the higher content of the fragments of aliphatic structures, carboxylic acids, alcohols, and esters, which ensures increased oxygen atom content in the structure of FA in comparison with HA. The data obtained in the investigation of FA and HA samples extracted from brown coal of the Tyulgan and Tisul deposits are in agreement with the results of investigation of the standard samples with FA and HA from peat (Pahokee Peat) and soil (Elliott Soil) of the Internationa Humic Society IHSS.

The data of EPR spectroscopy show that PMC concentration and the intensity of radical signal decrease as a sequence: BS > HA > FA. The value of g-factor 2.0023 for FA differs from g-factor 2.0034–2.0036 for BC and HA extracted from it, which is the evidence of differences in the nature of radicals. The presence of aroxyl semiquinone and phenoxyl radicals provides the paramagnetic properties of BC and HA.

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