

Composition of the Water-Soluble Humic Preparations of Mechanically Activated Brown Coals

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Abstract—Conditions for the solid-phase mechanochemical activation of coals, which make it possible to substantially increase the yield of water-soluble humic preparations enriched in humic acids and mineral elements, are given in this work. It was found that the humic preparations isolated from mechanically activated coals are characterized by an increase in the antioxidant activity and a change in the cationic and anionic composition. The concentration of acidic ionogenic groups in humic acids increased.

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The regulation of plant growth and development is one of the most important agricultural problems the solution of which will make it possible to considerably increase the productivity of crops and the safety of harvest and to simplify cultivation and agricultural processing technologies [1, 2]. Hundreds of compounds that possess high biological activity are synthesized every year on a global scale. As a rule, currently available synthetic growth regulators are not ecologically clean, and they are expensive; because of this, their applications are limited.

Among natural growth stimulators, the soluble salts of humic acids (HAs) with univalent metals, which are readily assimilated by plants, are characterized by a specific physiological effect. Different oxygen-containing functional groups (–COOH, –OH, etc.) enter into the composition of HAs; due to these groups, the structural fragments of HAs are bound to metals to increase the overall unspecific resistibility of plants and to intensify of the growth of first the root system and then the top [3, 4].

As a result of the stimulating action of HAs, the uptake of mineral elements in the form of cations and anions into plants through the root system is also intensified. In this case, the ions of particular metals enter into plants in a ratio different from that in a humic solution.

Traditional technologies for the production of humic preparations involve extraction with the large volumes of highly concentrated alkaline solutions on heating. This problem can be successfully solved as a result of the solid-phase transformation of humin-

containing raw materials after mechanochemical treatment with specially selected reagents [5–7]. Mechanochemical action makes it possible to increase the active surface area of the treated material to ensure the direct interaction of reagents with humic substances without a stage of their dissolution [8]. The yield of humic preparations after mechanochemical action becomes commensurable with their yield in usual alkaline extraction. However, the chemical composition of the resulting water-soluble humic preparations with mineral additives is scantily known.

The aim of this work was to develop a single-stage method for the production of water-soluble humic preparations enriched in mineral nutrition elements.

The initial humic acids were separated from oxidized (OC) and brown (BC) coals from the Ching-Chai and Chui-Kenul deposits (China) in accordance with the Instorf method [9] (OCHA and BCHA). The humic preparations were obtained from the initial coals (OCHP and BCHP) by the drying of alkaline extracts in a drying oven at a temperature of 30°C to constant weight.

The mechanoactivation (MA) of coals was carried out under the following conditions: the rotation frequency of drums was 1820 rpm, and the centrifugal acceleration was 600 m/s². The grinding bodies were steel balls with a diameter of 8–10 mm. The weight of balls in the load of a drum was 0.2–0.5 kg; the sample weight was 15–20 g, and the treatment time was 2 min. Coals were subjected to mechanical action without reagents (MA HA) and in the presence of a set of reagents, which were responsible for alkaline hydroly-

sis and the enrichment of HAs in mineral elements. The MA reagents had the following composition: coal, sand (in the case of OC treatment), NaOH, Na₄P₂O₇, and Na₂CO₃ · 1.5 · H₂O₂. The SiO₂ content of the sand was as high as 30 wt %. The ultrafine grinding of a mixture of coals in the presence of the alkaline reagents NaOH and Na₄P₂O₇ ensured the formation of a coal mechanocomposite in which the additive of sodium pyrophosphate enhanced the action of sodium hydroxide. As a result of the rupture of chemical bonds and alkaline hydrolysis reactions, the yield of humic substances increased by 30 wt %. The sodium percarbonate Na₂CO₃ · 1.5H₂O₂ is an oxidizing agent, which decreases the resinification of coal. The use of sand as an abrasive in the MA of oxidized coal is necessary for averting the agglomeration of coal particles containing cementing elements. This problem is absent from the MA of brown coal; therefore, the process was performed without sand additives.

Water-soluble humic preparations from mechano-activated coals with reagent additives were extracted with distilled water (MA OCHP and MA BCHP). The solutions obtained were centrifuged and filtered. Humic acids were separated by precipitation with HCl (4 wt %).

The quantitative determination of mineral elements in coals and humic preparations was carried out by atomic emission spectrometry¹ with the use of a high-resolution diffraction emission spectrometer. The test samples of 0.0500–0.1000 g were placed in preliminarily heated and weighed quartz crucibles; the 20- μ L portions of H₂SO₄ (concentrated) were added, and the contents were ashed in a muffle furnace to constant ash weight with a gradual increase in the temperature to 450–500°C. The cooled crucibles were weighed; graphite powder was added to the mineral residue to an initial sample weight, and the mixture was homogenized. The spectra were measured with the following parameters: direct current, 13 A; distance between the electrodes, 0.003 m; slit width, 3.0 × 10⁻⁵ m; diaphragm, 0.005 m; number of accumulations, 160; duration of accumulations, 125 ms; and total exposure, 20 s.

The concentrations of acidic ionogenic groups were determined by potentiometric titration. In the course of the titration of HAs, the ionic strength of solution was adjusted at a fixed level with a saturated solution of sodium chloride. In the resulting titration curves, three inflections were clearly recognized in the regions of pH 10–11 (phenol hydroxyls Ar–OH), pH 6.5–9.5 (carboxyl groups at the aromatic ring Ar–COOH), and pH 2.5–6.5 (carboxyl groups at hydrocarbon chains Alk–COOH). The equivalence points were calculated with the aid of numerical interpolation.

¹Grand instrument complex, NPO Optoelektronika, Russia.

The antioxidant properties of humic preparations were determined in accordance with a voltammetric technique by the cathodic reduction of oxygen with the use of a mercury film electrode. The supporting electrolyte was a phosphate buffer solution (pH 6.8). A weighed portion of the test sample (5 × 10⁻³ g) was dissolved in 5 mL of a 0.1 N solution of NaOH. The kinetic criterion K ($\mu\text{mol L}^{-1} \text{min}^{-1}$) of the antioxidant activity of the samples was calculated from the formula

$$K = \frac{C_0}{t} \left(1 - \frac{I}{I_0} \right),$$

where I is the electric reduction current of oxygen in the presence of an antioxidant in solution, μA ; I_0 is the electric reduction current of oxygen in the absence of the antioxidant from solution, μA ; C_0 is the initial concentration of oxygen in the solution, $\mu\text{mol/L}$ (it is equal to the solubility of oxygen in the test electrolyte under normal conditions); and t is the exposure time of the working electrode at a constant potential of the limiting current of oxygen.

The kinetic criterion reflects the amount of oxygen and active oxygen radicals reacted with an antioxidant (or total antioxidants) per minute of time [10–12].

The anionic and cationic compositions of water-soluble humic preparations were established by capillary electrophoresis. The method is based on the separation of the charged components of a complex mixture in a quartz capillary under the action of an applied electric field. The analyzed solution (a microvolume of ~2 nL) was introduced into a quartz capillary preliminarily filled with an electrolyte buffer solution. A solution of benzimidazole in tartaric acid with the addition of a solution of 18-crown-6 ether was used as a buffer electrolyte. After the supply of a high voltage (to 30 kV), a steady state was rapidly established in the capillary: a constant electroosmotic flow passed through the capillary and the mutually opposite electromigration of cations and anions was superimposed on it. The components of a mixture began to move with different speeds, which primarily depended on charge and mass, and correspondingly reached a detection zone at different times. The cations and anions were identified based on migration times in an electropherogram obtained with the aid of a photometric detector, and their concentrations were determined from the corresponding peak areas.

The main advantages of capillary electrophoresis consist in its high separation efficiency, the rapidity and simplicity of analysis, and low reagent consumption.

RESULTS AND DISCUSSION

Table 1 summarizes the characteristics of coals used for the production of humic acids and water-soluble humic preparations; these data indicate that the ash content of brown coal (29.9 wt %) was higher than

Table 1. Characteristics of the oxidized and brown coals

Coal	Ash content, wt %	Moisture content, wt %	Element concentration, wt %				
			Ca	Mg	K	P	Si
Oxidized coal	16.7	16.8	0.25	0.082	0.03	0.14	0.35
Brown coal	29.9	6.7	0.45	0.14	0.05	0.10	0.60

that of oxidized coal (16.7 wt %) and the moisture content was lower. The ash and moisture contents of coals exert an effect on the yield and composition of HAs after MA. The radicals formed under mechanical action in moist samples interacted with water molecules; this interaction can lead to a decrease in the length of a molecular chain. Recombination processes with the formation of larger molecules can occur on the grinding of dry coal samples.

The Ca and Mg contents of the initial brown coal are higher by a factor of 1.7–1.8 than that of the initial oxidized coal (Table 1). The polyvalent cations contained in coals can interact with HAs in the MA process to form connecting bridges between the macromolecules and to decrease the solubility of HAs.

The water-soluble humic preparations obtained as a result of the extraction of mechanoactivated coals are the salts of humic and fulvic acids. Figure 1 shows that the yields of water-soluble MA OCHP and MA BHP were 84.2 and 61.3 wt %, respectively. The high concentration of mineral components (to 30 wt %) in brown coal does not make it possible to further increase the yield of a water-soluble humic preparation.

It was established that the HA amount extracted from coals upon mechanochemical treatment was 30–47 wt % greater than that obtained in accordance with the Instorf procedure (Fig. 1). The amount of HAs in the composition of water-soluble humic preparations differed by 4–5 wt % from their total yield after the MA of coals.

The concentration of acidic ionogenic groups in the humic acids modified by the MA of coals increased due to an increase in the number of hydroxyl (ArOH) and carboxyl (ArCOOH) groups in the aromatic ring (Table 2).

The quantity of carboxyl groups at the ends of the HA hydrocarbon chains after modification remained almost unchanged. An increase in functional groups in the composition of HAs ensures an increase in the absorption capacity for cations, which is an important characteristic of the complex-forming ability of HAs. In the case of water-soluble humic preparations, both humic acids and fulvic acids participate in the absorption of cations as a result of exchange reactions to form organomineral compounds [13].

Under the conditions of oxygen deficiency, atmospheric oxygen as an electron acceptor can be replaced by its analogs. The presence of oxygen-containing functional groups and different cations and anions in

HAs facilitates electron and proton transfer as a result of redox reactions. Under certain conditions, HAs serve as the inhibitors of an oxygen reduction process. The antioxidant (redox) activity of HAs was evaluated based on the kinetic criterion K (Table 2). The humic acids obtained from oxidized coal were characterized by higher antioxidant activity, which was comparable with that of other highly active natural antioxidants. For comparison, the antioxidant activity K of quercetin was $0.27 \mu\text{mol L}^{-1} \text{min}^{-1}$ at a concentration of $1.55 \times 10^{-6} \text{ mol/L}$, as determined by voltammetry using the cathodic reduction of oxygen. The mechanoactivation of coals with mineral reagents led to an increase in the values of K for humic acids by 12–20%.

The concentrations of the following bound macro and trace elements in the ashes of initial HAs and in the HA samples after the MA of coals were determined by atomic emission spectrometry: Mg, Ca, P, and Si (Table 3). The comparative analysis showed that the MA of coal with the addition of reagents ensured the enrichment of humic acids in calcium by a factor of 2 or 9 in the case of oxidized coal or brown coal, respectively. The MA BCHA were also characterized by an increase in the fraction of magnesium by a factor of 5, as compared with the initial sample. The mechanical treatment of coal samples in the presence of sodium pyrophosphate also facilitated the enrichment of HAs in phosphorus by a factor of 10 regardless of the origin of test coal.

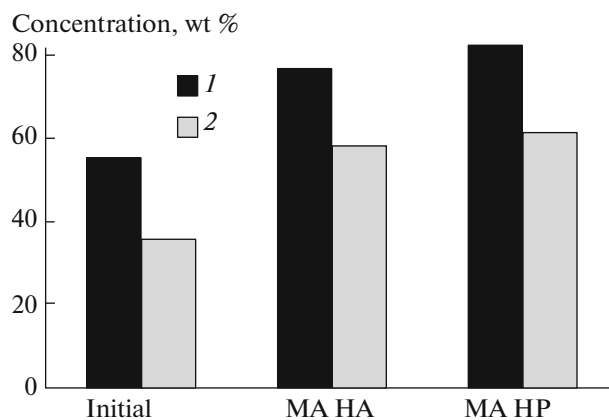


Fig. 1. Yields of humic acids and water-soluble humic preparations from the initial coals and after mechanical treatment with mineral additives: (1) oxidized brown coal and (2) brown coal.

Table 2. Concentrations of acidic ionogenic groups in humic acids and the antioxidant activity (*K*)

Sample	Concentration of functional groups, mg-equiv/g			Antioxidant activity <i>K</i> , $\mu\text{mol L}^{-1} \text{min}^{-1}$
	C _n COOH	ArCOOH	ArOH	
OCHA	2.1	5.8	8.6	0.30
BCHA	2.3	6.2	9.9	0.28
MA OCHA	2.5	6.1	9.3	0.37
MA BCHA	2.4	7.3	11.3	0.32

Table 3. Concentrations of macro and trace elements in humic acids according to the results of atomic emission spectrometry

Element	Concentration, wt % $\times 10^{-3}$			
	OCHA	BCHA	MA OCHA	MA BCHA
Ca	11	4.5	23	40
Mg	11	3.8	12	20
P	11	7	110	70
Si	57	12	300	60

Table 4. Anionic and cationic compositions of the initial humates and water-soluble humic preparations from the oxidized and brown coals after mechanical treatment

Ion	OCHP	BCHP	MA OCHP	MA BCHP
	extraction with 0.1 N KOH		extraction with 0.1 N NaOH	
Anionic composition, mg/g $\times 10^{-3}$				
SO ₄ ²⁻	9.8	5.5	6.6	12.4
NO ₃ ⁻	0.2	0.5	2.9	10.9
F ⁻	0.09	0.03	0.06	0.1
PO ₃ ⁻	0.5	0.2	11.5	7.7
HCO ₃ ⁻	5.8	6.1	6.8	5.6
Cationic composition, mg/g $\times 10^{-3}$				
K ⁺	97.7	128.6	0.7	ND
Na ⁺	12.3	34.0	70.8	119.1
Ca ²⁺	3.7	4.0	4.7	14.5
Mg ²⁺	0.8	0.7	1.2	2.3

The determination of silicon in HAs is of considerable interest. Filippova et al. [14] found that the use of silylated humic preparations as bioactivators is promising under salt stress conditions. Silicon occurs in

oxidized coal and brown coal in concentrations of 0.35 and 0.60 wt %, respectively (Table 1). An insignificant silicon content was detected in humic acids isolated from unprocessed coals (Table 3). Experiments on the mechanical treatment of oxidized coal and brown coal showed their different ability to experience mechanical action. For the mechanical treatment of oxidized brown coal, which is characterized by an amorphous structure, an abrasive should be used to prevent the agglomeration of particles. The use of a silicon-containing material in the MA of oxidized coal increased the silicon content of HAs from 57×10^{-3} to 300×10^{-3} wt %. According to the data of Table 3, it is evident that the MA of brown coal was also accompanied by an increase in the silicon content of HAs due to a redistribution under mechanical action.

For using the water-soluble humic preparations as the sources of mineral nutrition components for plants, it is necessary to determine the ionic composition of macro and trace elements because they are supplied in the form of cations and anions. The ionic composition of humic preparations was established by capillary electrophoresis.

Figure 2 shows the electropherograms of the anionic and cationic compositions of a humic preparation from the initial brown coal. Among the cations, the ions K⁺ and Na⁺ were predominant, and the ions Mg²⁺ and Ca²⁺ were present in smaller amounts. The anionic composition included SO₄²⁻, NO₃⁻, PO₄³⁻, HCO₃⁻. The fluoride ion was detected in a negligibly small quantity.

Table 4 summarizes the concentrations of anions and cations detected in humates from the initial coals (OCHP and BCHP) and the water-soluble humic preparations (MA OCHP and MA BCHP). The high concentration of potassium ions in the former case and sodium ions in the latter case were caused by the method of humate extraction from coals with the solutions of KOH and NaOH, respectively.

Magnesium ions occurred in insignificant quantities in the initial humic preparations obtained by alkaline extraction with KOH. After the MA of coals, the concentrations of Mg²⁺ and Ca²⁺ ions in the water-soluble humic preparations MA OCHP and MA BCHP increased by a factor of 2–3. The enrichment of preparations in the above ions manifested itself to a larger degree upon the MA of brown coal. It is likely that an increase in the concentrations of magnesium and calcium ions was related to a redistribution of these elements in the course of the MA of coals with the addition of reagents (Table 1).

The anionic composition of humic preparations also underwent quantitative changes after the MA of coals, which can be caused by both the occurrence of mechanochemical reactions and the composition of the utilized reagents.

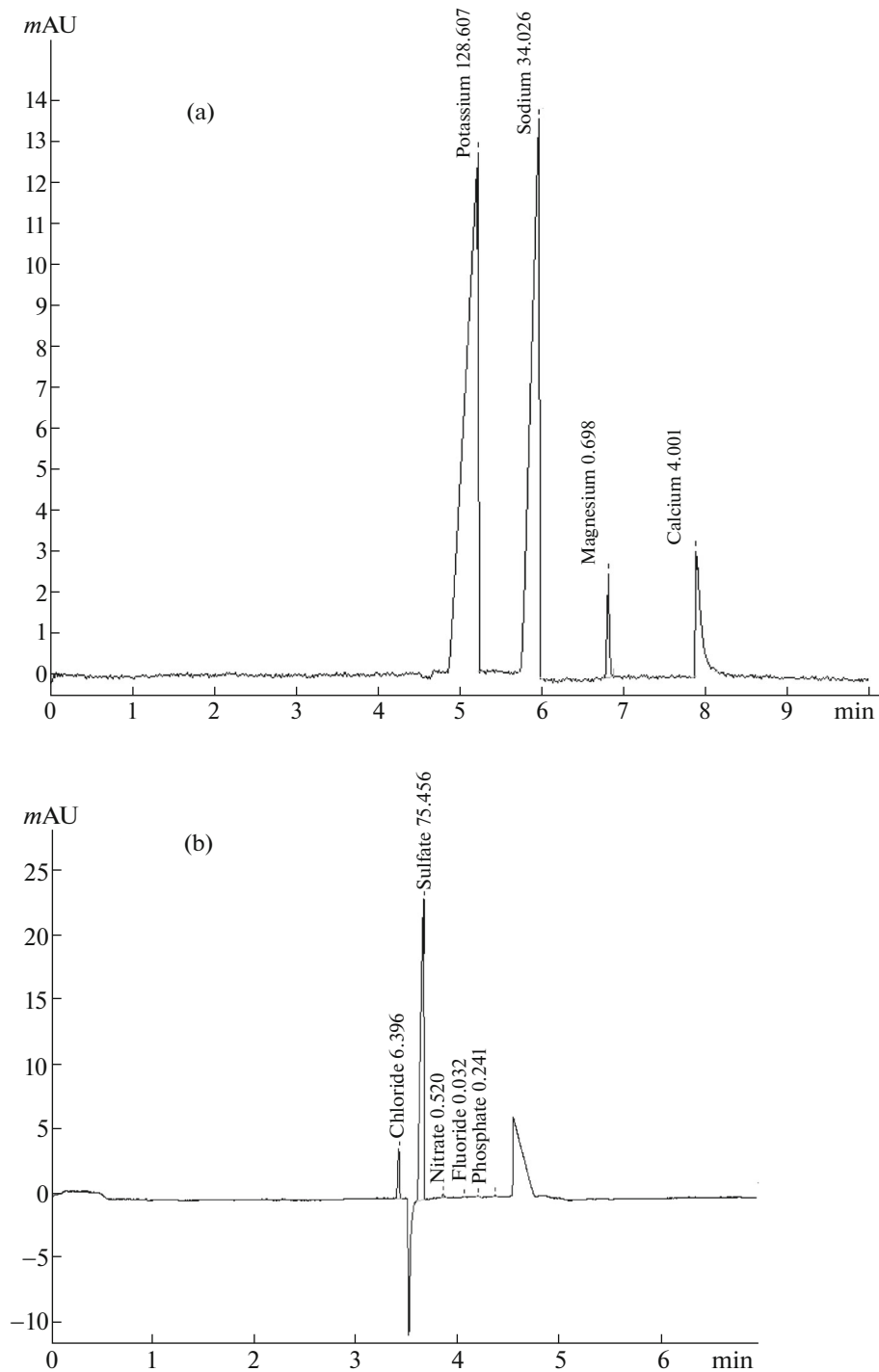


Fig. 2. Electropherograms of the (a) cationic and (b) anionic compositions of humic preparations from brown coal.

Note that the concentration of free SO_4^{2-} ions in the mechanoactivated samples decreased, especially, in the case of MA BCHP. The increase in the amounts of NO_3^- and PO_4^{3-} in the water-soluble humic preparations by factors of 15–20 and 22–30, respectively, as compared with the initial samples, is indicative of an

essential positive effect of selected additive concentrations in the MA of coals.

The analysis of the results of the quantitative determination of elements such as Ca, Mg, and P in HAs obtained by capillary electrophoresis showed that mechanoactivation facilitated the enrichment of water-soluble humic preparations in mineral macro

and trace elements, which are necessary for the growth and development of plants and the overcoming of stress conditions.

CONCLUSIONS

Conditions for the solid-phase mechanochemical activation of coals were optimized in order to substantially increase the yield of water-soluble humic preparations to 61.3 (brown coal) and 84.2 wt % (oxidized coal) enriched in humic substances and mineral elements, as compared with the unprocessed samples. It was shown that the MA of coals leads to an increase in the total quantity of acid ionogenic groups in the composition of HAs. Humic preparations were characterized by an increase in the antioxidant activity and by a change in the cationic and anionic composition: the concentrations of the ions Mg^{2+} and Ca^{2+} , NO_3^- , and PO_4^{3-} increased by factors of 2–3, 15–20, and 22–30, respectively. It was established that the silicon content of HAs increased by a factor of 5 upon the mechanical treatment of oxidized coal with the addition of a silicon-containing abrasive material.

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