Variation of the Composition and Properties of the Water-Soluble Components of Peat during Mechanochemical Treatment

OLEG I. LOMOVSKY[1], ALEXANDER A. IVANOV[2], OLGA A. ROZHANSKAYA[3], NATALIA V. YUDINA[2] and KONSTANTIN G. KOROLEV[1]

[1]Institute of Solid State Chemistry and Mechanochemistry, Siberian Branch of the Russian Academy of Sciences, Ul. Kutateladze 18, Novosibirsk 630128 (Russia)

E-mail: lomov@solid.nsc.ru

[2]Institute of Petroleum Chemistry, Siberian Branch of the Russian Academy of Sciences, Prospekt Akademicheskiy 3, Tomsk 634055 (Russia)

[3]Siberian Scientific Research Institute of Fodder, Siberian Branch of the Russian Academy of Agricultural Sciences, Novosibirsk region, pos. Krasnoobsk 630501 (Russia)

Abstract

Variation of composition and properties of the water-soluble components of peat during mechanochemical treatment has been studied. Mechanochemical treatment affects the composition, quantitative content, and biological activity of the water-soluble components of peat. Mechanochemical treatment of high peat with celloviridine and alkali increases the yield of the water-soluble oxygen-containing compounds, including humic acids. The mineral composition of peat after processing practically did not change. The water-soluble components obtained by the mechanochemical method stimulate germination of seeds and development of wheat sprouts at the early stages of vegetation.

INTRODUCTION

Seeking ecologically safe and economically efficient methods for processing of natural organic raw materials has become a crucial problem. The wide use of peat [1] in chemical engineering, agriculture, and medicine has stimulated research on methods for integrated processing of this raw material. One of the key problems in peat processing is activation of extraction of extractives such as humic acids, fulvic acids, phenols, polysaccharides, and other compounds of practical interest.

For complete extraction of target components, one uses multiple treatment of raw material with solvents of varying polarity. The drawbacks of the conventional extraction technology are the use of toxic and fire-dangerous organic solvents, low degree of extraction, repeated extraction, and hence increased production costs and pollution of environment.

The extraction rate, as well as the yield of the end products, is controlled by solvent diffusion. The use of preliminary mechanical activation makes it possible to attain peak efficiency at the stage of subsequent extraction. Impact shear treatment is accompanied by fragmentation and structure disordering of the material. This considerably facilitates isolation of components. Thus, for example, mechanical treatment of a mixture of bark and solid alkali powders enables one to obtain a composite with a developed phase boundary. The microparticles of solid alkali are distributed in the bulk of the plant material with a disturbed cellular structure. Addition of water to this composite allows one to isolate the maximum quantity of water-soluble compounds in a single-stage process without preliminary degreasing [2]. Direct aqueous extraction of the bark, which contains insoluble lipids and resinous components, is inefficient.

Increased dispersity of the raw material results in increased yields of ballast substances after extraction. This problem may be solved by combining dispersion with modification of the target or ballast substances of the plant raw material. This approach is called "solid-phase mechanochemical extraction" and consists in reactive crushing of raw material [3]. The technology includes the stage of mechanochemical treatment of the powder mixtures composed of a plant raw material and a specially selected solid phase. For the latter one uses "collectors" (adsorbents of varying chemical nature) or "reagents" (compounds capable of reacting with target or ballast substances). Since crushing is accompanied by an increase in the total contact surface, the substances of the raw material can be combined with the "collector" or enter chemical reactions with the "reagent" [4, 5].

Thus, mechanochemical treatment not only increases the effective surface of the components (apart from removing or reducing the problems encountered by diffusion), but it also induces chemical transformations of the target substances into forms having the highest solubility in water or other solvents. From the obtained mechanocomposite it is generally possible to selectively isolate the target compounds in maximum yields, normally achieved by prolonged continuous extraction.

Previously, it has been shown that vigorous mechanical activation of peat is accompanied by changes in the properties of the high-molecular component and results in increased yields of extractive products [6, 7]. Despite great progress in the field of mechanochemical treatment of natural organic raw materials, detailed investigations of mechanochemical treatment of peat using a system of modern physical and chemical methods have not yet been performed. The purpose of the present work is to study the effect of mechanochemical treatment on the composition of peat and on the content and biological activity of the water-soluble components.

EXPERIMENTAL

Two kinds of peat were chosen as research objects: high-moor peat from the Temnovoye deposit attributed to the moss group with low percents of decomposition (5 %) and ash content (3.7 %), and low-moor peat of the Taganskoye deposit belonging to the wood group with high percents of decomposition (30 %) and ash content (25 %).

Peat treatment was performed in a VTsM-10 flow-type vibrocentrifugal activator (designed at the Institute of Solid State Chemistry and Mechanochemistry, SB RAS, Novosibirsk). Steel spheres 10 mm in diameter were used as milling agents. Acceleration of spheres was 180 m/s^2. Residence time of the material in the active zone was 2 min.

An attempt has been made to increase the efficiency of isolation of the water-soluble components by combining mechanical activation with the action of alkali and ferment on peat. Mechanochemical treatment in the presence of an alkali makes it possible to perform chemical reactions forming water-soluble compounds of the acid part. A cellulolytic enzyme celloviridin was added to the system during mechanical treatment to break the cellulose and hemicellulose skeleton and to increase the yield of the products of mechanochemical reactions (soluble carbohydrates and noncarbohydrate compounds previously bonded with cellulose).

To study the general properties of peat we used the standard techniques for determining the botanical composition and the degree of decomposition [8]. The ash content was determined in accordance with GOST 11306–83 [9].

The element composition of the peat samples was determined with a Carlo Erba Strumentazione analyzer, model 1106 (Italy). The content of mineral elements was determined by the X-ray fluorescent method [10].

The group composition of peat was investigated according to the scheme described in [11]. Lipids, polysaccharides, polyphenols, and humic acids were isolated from the starting and processed peat according to the following scheme. The water-soluble components (polysaccharides and polyphenols) were sequentially removed from the air-dried samples by using hot water (95 °C), and then lipids were isolated by extraction with chloroform. Humic substances were extracted with a 0.1 M NaOH solution, and humic acids were precipitated by treatment with a 4 % solution of HCl, then washed with distilled water to pH 6.5–7, and dried in a vacuum chamber at ambient temperature.

RESULTS AND DISCUSSION

Effect of mechanoactivation on the composition of peat and the yield of the water-soluble components

The element composition of the peat samples under study varies according to the processing conditions (Table 1). This may be caused by reactions occurring during mechanochemical treatment, accompanied by evolution of gaseous products, for example, ammonia and carbonic gas. As shown by the element analysis, the carbon content in peat is 46.7–53.7 %, the hydrogen content varies from 5.7 to 7.6 %; the content of nitrogen in peat varies from 0.33 to 4.2 mass %, and that of oxygen, from 37.6 to 46.3 mass %. The amount of carbon increases in low-moor peat after mechanical treatment with reagents, while the content of nitrogen decreases; in high-moor peat, the content of oxygen increases.

The H : C, O : C, and C : N ratios were employed for evaluating the processes of transformation of the organic matter. The H : C ratio decreased compared to reference values in samples of peat after mechanical treatment without additives. As shown in [12], dispersion of air-dried samples leads to processes resulting in the formation of condensed structures from some peat components. Mechanical treatment with alkali and celloviridin reduces the probability of molecular integration and increases the H : C ratio. Based on the O : C and N : C ratios one can infer that the content of oxygen-containing compounds increases in high-moor peat after mechanical treatment with an alkali and a ferment, while the fraction of nitrogen compounds in low-moor peat decreases.

The iron content, affecting the reactivity of the fractions, is an important chemical characteristic of the product of mechanical activation of peat. As shown by X-ray fluorescence analysis, the metal and silicon contents in the processed samples differ from those in the original samples within the error of the analytical method (Table 2). Hence, during mechanochemical treatment in a VTsM-10 mill the organic matter of peat does not react with the material of the mechanical activator.

Mechanical activation of peat in the presence of reagents changes the yield and qualitative characteristics of the basic components isolated from it. The character of the observed changes depends on the type of peat and conditions of mechanical treatment. Figure 1, *a*, *b* shows the group compositions of peat of both types. Analysis of the initial and mechanochemically processed samples of peat

TABLE 1

Element composition of peat and atomic ratios of elements

Conditions of mechanical treatment (additive)	Content, mass %				Atomic ratio		
	C	H	N	O	H : C	N : C	O : C
			High-moor peat				
Source peat	48.1	5.9	0.65	44.2	1.47	0.01	0.69
Without reagent	48.1	5.7	0.62	44.6	1.42	0.01	0.69
0.5 % celloviridin	47.1	6.7	0.33	45.8	1.71	0.006	0.73
3 % NaOH	46.7	6.6	0.34	46.3	1.69	0.01	0.86
0.5 % celloviridin + 3 % NaOH	47.5	6.5	0.69	45.3	1.64	0.01	0.71
			Low-moor peat				
Source peat	50.6	7.2	4.2	37.9	1.70	0.07	0.56
Without reagent	52.6	6.5	3.1	37.8	1.49	0.05	0.53
0.5 % celloviridin	53.7	7.4	1.2	37.6	1.65	0.02	0.52
3 % NaOH	50.8	7.3	3.3	38.6	1.72	0.05	0.57
0.5 % celloviridin + 3 % NaOH	51.7	7.6	2.2	38.5	1.76	0.04	0.56

TABLE 2

Change in the mineral composition of peat after mechanochemical treatment

Treatment conditions (additive)	Content of elements in peat, mass %			
	Fe	Mn	Ti	Si
High-moor peat				
Source peat	1.10	0.065	0.10	Traces
Without reagent	1.21	0.067	0.11	»
0.5 % celloviridin	1.18	0.065	0.10	»
3 % NaOH	1.08	0.064	0.10	»
0.5 % celloviridin + 3 % NaOH	1.10	1.066	0.10	»
Low-moor peat				
Source peat	6.67	0.185	0.279	6.77
Without reagent	6.75	0.156	0.267	6.70
0.5 % celloviridin	6.72	0.148	0276	6.42
3 % NaOH	7.54	0.153	0.267	6.70
0.5 % celloviridin + 3 % NaOH	6.53	0.159	0.278	6.92

showed that the content of lipids (L) decreases irrespective of the kind of peat and treatment conditions. The content of lipids in high-moor peat with an alkali addition decreases to a greater extent than in the presence of celloviridin (see Fig. 1, *b*).

After mechanical treatment, the amount of water-soluble substances (WS) increased five- to tenfold in both kinds of peat compared to the original samples. The maximal yield of WS is reached for high-moor peat with celloviridin; addition of an alkali reduces the amount of isolated WS. On the contrary, for low-moor peat, larger yields of WS were observed with an alkali addition, which is associated with the formation of water-soluble humates.

Dispersion in the presence of a ferment increases the yield of humic acids (HA), while mechanical treatment in the presence of an alkali tends to decrease it. For samples obtained by mechanochemical processing of peat, the increased yield of HA is probably due to the destruction of substances that are not readily hydrolyzable. Mechanochemical processing in the presence of an alkali results in abruptly decreased amount of HA owing to the formation of water-soluble humates.

During mechanical processing, the ratio of the isolated water-soluble fractions (polysaccharides and polyphenols, Table 3) changes.

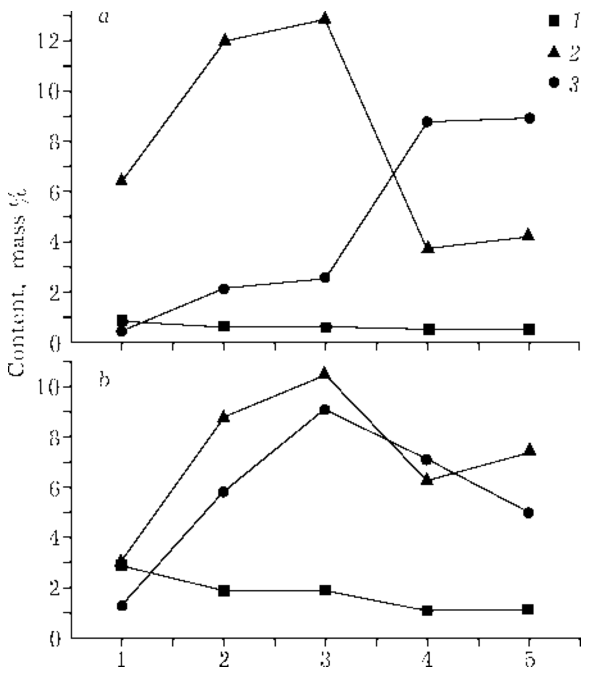

Fig. 1. Dependence of the content of lipids (*1*), humic acids (*2*), and water-soluble substances (*3*) in low-moor peat (*a*) and high-moor peat (*b*) on conditions of mechanical processing: 1 – source peat, 2 – peat after mechanical processing without additives, 3 – mechanical processing with 0.5 % celloviridin, 4 – mechanical processing with 3 % NaOH, 5 – mechanical processing with 3 % NaOH + 0.5 % celloviridin.

TABLE 3

Effect of mechanical processing on the yield and composition of the water-soluble substances of peat

Conditions of mechanical	Content, mass %	
processing (additive)	Polysaccharides	Polyphenols
	High-moor peat	
Source peat	0.2	1.1
	2.4	3.4
0.5 % celloviridin	2.9	6.1
3 % NaOH	4.3	2.7
0.5 % celloviridin + 3 % NaOH	0.7	4.3
	Low-moor peat	
Source peat	0.1	0.3
Without reagent	0.4	0.9
0.5 % celloviridin	1.0	1.5
3 % NaOH	0.7	8.1
0.5 % celloviridin + 3 % NaOH	0.6	8.3

High-moor peat processed with a ferment contains the maximum amount of soluble polyphenols. During alkaline hydrolysis, the content of extracted polyphenols decreases considerably compared to that of the initial samples, while the amount of water-soluble polysaccharides increases. The efficiency of alkaline hydrolysis may be raised by adding a ferment during mechanical treatment.

Effect of peat stimulants on seed germination and development of wheat sprouts at early stages in the pot experiment

Plant growth and development regulation is one of the most important problems in modern science from both theoretical and practical viewpoints. On the one hand, it is closely related with the central problem of biology concerning the mechanisms of ontogenesis regulation and the differential activity of genes. On the other hand, utilization of growth regulators in agriculture considerably increases the efficiency and safety of crops, and leads to simpler technologies of cultivation and processing of agricultural production [13, 14].

To study the characteristics of external factors one uses biological objects with well-investigated properties, *i.e.*, biotests [15]. Field survey is the most widespread method for evaluating various plant growth stimulants and to reveal how the external factors affect the productivity.

For peat stimulants, we chose water-soluble substances after mechanical activation of high- and low-moor peat with a ferment (samples H2, L2, Table 4) and with an alkali (samples H3, L3). The samples (10 mg/l) were dissolved in hot distilled water.

A pot experiment involved sprouting wheat seeds in solutions of the substances under study and regular measurements of sprouts in the first 10 days of their growth. The early stages of ontogenesis, as a rule, correlate with the later parameters of plant development and efficiency, which allows the use of sprouts as biotests. Wheat seeds of “Kantegirskaya-89” and “Novosibirskaya-89” breeds were used as research objects.

The wheat seeds were placed in rolls of filter paper and allowed to germinate in solutions of the substances under investigation for 10 days. During the experiment, the height of shoots and the length of roots were measured; the germinating power and germination of seeds were taken into consideration. At the end of experiments, the sprouts were weighed. The results of experiments are presented in Table 4 and Fig. 2.

TABLE 4

Effect of growth regulators on germination of wheat seeds. H2, H3 and L2, L3 are water-soluble substances from high- and low-moor peats respectively after mechanical activation with a ferment and an alkali

Run version	Germinating power (3 days), %	Germination, %	Raw mass of 30 seeds at the end of experiment	
			g	% of values for test samples
Test samples (without additives)	80	90	3.78	100
H2	72	86	3.78	100
H3	83	87	4.52	120
L2	87	97	4.14	110
L3	97	97	4.15	110

The results of experiments were processed by methods of dispersion analysis and by means of nonparametric criteria of statistics [16].

Germination of seeds starts with the appearance of a little root, then the stalk starts to grow. The germination and the germinating power of seeds increased in runs with L2 and L3 additives (see Table 4).

The average length of pedicle in two-day sprouts increased reliably in runs with H3, and the length of little root increased in all variants with all additives except H2 (see Fig. 2). A statistically reliable (at a level of 1 %) increase in the height of shoots was recorded for six-day sprouts in the presence of H3, L2. The roots slowed down their growth in the H3 variant, and in the L2 variant, the values considerably exceeded the test values. L3 provided a gain of 60 % for the height of shoots, 40 % for the length of roots, and 20 % for the mass of sprouts. The stimulating effect of H3 and L3 additives was less distinct, although statistically reliable.

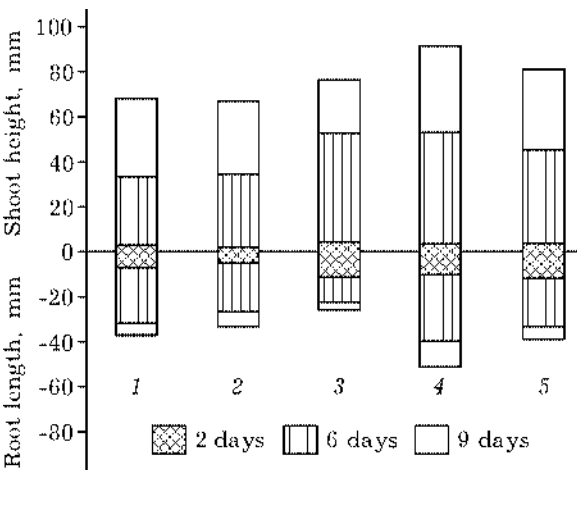

Fig. 2. Effect of growth regulators on growth of wheat shoots and roots: *1* – test experiment; *2* – H2, 10 mg/l; *3* – H3, 10 mg/l; *4* – L2, 10 mg/l, *5* – L3, 10 mg/l.

As a result of pot experiments, it was established that:

– The preparation obtained by alkaline hydrolysis of high-moor peat and characterized by increased concentrations of water-soluble substances stimulates growth of wheat shoots and increases their mass; the preparation obtained by enzymatic hydrolysis and characterized by lower contents of water-soluble substances but higher contents of humic acids does not display any activity.

– The preparation obtained in the presence of an alkali and a ferment has a significant stimulating effect on growth of wheat shoots; the preparation obtained by treatment in the presence of a ferment and characterized by the maximal content of water-soluble substances and humic acids has the maximum activity.

CONCLUSIONS

Studies on mechanochemical treatment of high- and low-moor peat have been reviewed. Mechanochemical treatment of different kinds of peat in the presence of an alkali and a cellulolytic enzyme increases the yield of the water-soluble fractions by a factor of 5–10; the yield of humic acids also increases, while the yield of lipids decreases.

The biostimulating action of peat preparations on germination of wheat seeds has been studied. Preparations with increased concentrations of water-soluble substances of low-moor peat have been shown to produce a considerable stimulating effect.

Acknowledgement

This work was supported by the Russian Fund for Basic Research (project 03-03-32250) with the assistance of the American fund of support for basic research CRDF (grant NO-008-XI).

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