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## Changes in the Chemical Composition of the Major Components of Peat under Cavitation Action

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### Abstract

Changes of the quantitative and qualitative characteristics of peat components (bitumen, lignin, cellulose, humic acids) under cavitation action of aqueous alkaline media are considered. It was demonstrated that the cavitation treatment of peat in alkaline solutions involves the structural rearrangement, changes of separate fragments of macromolecules. As a result, additional amount of humic acids is formed. To obtain humic acids, it is preferable to use the aqueous solution of ammonia as the base. In water-ammonia medium, nitrogen fixation occurs with the participation of all the components of humate-carbohydrate complex.

**Key words:** peat, humic acids, humification

### INTRODUCTION

Mechanochemical methods are increasingly frequently used to obtain and extract humic acids (HA) from plant raw materials (peat [1], wood chips [2]) [3, 4]. Isolation of HA from traditional kinds of raw material is based on extraction with water-alkaline solutions, so the most promising direction of studies is connected with the use of ultrasonic or cavitation action.

Cavitation is the formation of the vapour and gas phase in the form of microscopic bubbles (cavities) in the liquid medium. Cavitation may be produced artificially as a result of superfast liquid flow along the pipe profile of variable cross section. Local destruction of intermolecular interactions in the solvent due to the flow of this kind leads to the formation of the vapour and gas phase at temperatures below the phase transition point. The short lifetime of a cavity in liquid flow is due to a collapse, which generates strong hydrodynamic perturbations in the liquid and

intense generation of acoustic waves in the ultrasonic region [5].

The resonance of acoustic waves generated by cavitation and the chemical bonds of molecules in the plant raw material dispersed in the liquid phase may cause the destruction of these bonds thus initiating new chemical reactions. Along with this, the molecules of polar media, such as water, under the action of cavitation undergoes homolytic decomposition with the formation of a number of free radicals such as  $\text{OH}^\bullet$ ,  $\text{O}^\bullet$  etc. [6]. These radicals and the products of their recombination (for example,  $\text{H}_2\text{O}_2$ ) may initiate oxidation processes involving the molecules of the plant raw material. So, water in the cavitation process is not only the medium but also the source of oxidizing agent ( $\text{H}_2\text{O}_2$ ). In addition, free radicals generated in the medium may transfer their paramagnetic centres to the polymer molecules of the raw material.

Under the action of ultrasonic cavitation, the reactions of mechanochemical origin are accelerated. These reactions include deforma-

tion, rupture of intermolecular chains to form separate fragments, formation of active radicals, dissociation of molecules, the formation of superoxides, hydrogen peroxides, complexes like  $(\text{H}_2\text{O} \cdot \text{O}_2)(\text{OH} \cdot \text{O}_2)$ , hydrated electrons. At the same time, specific acoustochemical reactions are initiated; these reactions are based on the mechanism of rupture of chemical bonds [6]. So, the use of cavitation may lead to the changes of the chemical structure of a substance.

The goal of the present study was to reveal the most general changes in the chemical composition of the major components of peat subjected to cavitation action of water-alkaline media.

## EXPERIMENTAL

The object of investigation was high-moor oligotrophic peat from the Ob-Irtysh floodplain. The decomposition degree of peat (*R*) was equal to 20 %.

A weighted portion of peat was treated with the alkaline solution of 1 mol/L for 10 min in a rotor cavitation apparatus designed by A. D. Petrakov [7], with the rotor frequency of  $3000 \text{ min}^{-1}$ , and then the resulting mixture was separated by centrifuging. Humic acids were precipitated from the liquid phase by acidifying with 10 % sulphuric acid to pH 2. Further operations were carried out according to the procedure described in [8].

The solid residue was examined for the concentrations of bitumen [9], cellulose (using Kurschner's method), and lignin (using Komarov's method) [10]. To study the qualitative characteristics of lignin, it was extracted with dioxane [10].

The elemental composition of the substances was studied using a Carlo Erba Strumentazione CHN analyser, model 1106 (Italy).

## RESULTS AND DISCUSSION

Cavitation treatment of peat results in the changes of the yield and qualitative characteristics of the major components of peat (Table 1).

Cavitation treatment in water-alkaline medium causes a substantial decrease in the concentrations of bitumen, lignin and cellulose. A decrease in the fraction of bitumen may be explained relying on the structure of bitumen molecules which are glycolipids. Hydrophobic by their nature, bituminous molecules incorporate the ester bond which is prone to alkaline hydrolysis. As a result, two hydrophilic molecules are formed; they pass into solution. In addition, alcohol groups that are present in bitumen are also prone to oxidation, which enhances hydrophobic properties [11].

The transformations of this kind affect the whole humate-carbohydrate complex of peat. For example, cellulose is prone to hydrolysis of glycoside bond from the reducing end and to oxidation of primary hydroxyl groups. Lignin of peat is also prone to oxidation and hydrolysis.

An increase in the fraction of HA is due to two opposite processes of destruction and condensation. Evidently, mechanocracking process is possible in the reactor [12]. In this situation, destruction of the polymer molecules of polyose and lignin has a random character and is not always accompanied by the destruction of lignocarbon bonds. Mechanocracking leads to the

TABLE 1

Concentrations of the major components of peat subjected to cavitation action in the aqueous solutions of alkalis

Components	Concentrations, %			
	Initial peat	After cavitation treatment in the solution of:		
		NH <sub>3</sub>	NaOH	KOH
Bitumen	10.6±0.6	3.0±0.9	2.2±0.8	3.6±1.1
Lignin	37.3±1.4	16.5±0.3	10.2±1.1	8.5±0.9
Cellulose	15.9±1.3	5.6±0.9	6.8±1.5	6.1±1.8
Humic acids	19.9±3.1	51.2±1.2	51.8±3.9	52.4±2.3

TABLE 2

Elemental composition of bitumen after cavitation treatment in different aqueous solutions of alkalis

Peat samples	Element content, %				H/C	N/C	O/C
	C	H	N	O			
Initial	76.27±0.35	11.46±0.04	0.32±0.01	11.95	1.8	$6.5 \cdot 10^{-3}$	0.12
Treated in NH <sub>4</sub> OH	78.12±0.15	11.75±0.07	0.43±0.08	9.71	1.8	$4.8 \cdot 10^{-3}$	0.09
the same, in NaOH	79.46±0.18	11.87±0.01	0.47±0.02	8.20	1.8	$5.1 \cdot 10^{-3}$	0.08
the same, in KOH	77.39±0.01	11.37±0.04	0.59±0.02	10.65	1.8	$6.5 \cdot 10^{-3}$	0.10

formation of free macroradicals [12]. Phenols are used as inhibitors of oxidative processes [13] because the lifetime of aryl and phenyl radicals is much longer than that of alkyl radicals. It may be stated that the condensation of macroradicals proceeds through the interaction of free radical states localized at the phenyl propane ends of the interacting particles. In other words, lignin fragments undergo condensation through the formation of C–C bonds thus forming the core part of HA molecules. Because polyose fragments are present also in the interacting macroradicals, the peripheral part of HA molecule in the form of numerous polyose tails is formed simultaneously with the formation of the core part.

To achieve better understanding of the changes that occur in the chemical composition of peat, we studied the elemental composition of its major components (Tables 2–5).

The degree of bitumen oxidation, characterized by the O/C ratio, increases depending on the strength of the base (see Table 2). The fraction of nitrogen fixation by the molecules of bituminous substances is also dependent on electrolyte strength. An increase in the fraction of elemental nitrogen along with a decrease in H/C ratio is the evidence that condensation processes occur in bituminous molecules, and an additional amount of carbon-carbon bonds is formed.

Characterizing the elemental composition of cellulose extracted from peat (see Table 3) it is necessary to stress that the elemental composition of initial cellulose is far from being similar to the composition of the polymers of this kind extracted from other plant materials. First of all, the presence of elemental nitrogen in the polymer should be stressed, as well as extremely low carbon content and high oxygen content.

It is likely that the molecule of polyose under investigation is strongly oxidized at the primary and (or) secondary hydroxyl groups of the glycoside ring. A part of the formed carboxylic and carbonyl groups have entered the reaction with ammonium ion.

Evidently, cavitation treatment in water-ammonia medium is oxidative aminolysis (OA) of the humate-carbohydrate complex. It may be stated with a high probability that OA leads to nitrogen binding by the carboxylic group of the glucuronic fragment of polyose. These assumptions and the experimental data are in good agreement with the results of previous studies [14].

The invariance of the atomic ratios of H/C also points to the prevailing oxidation of primary hydroxyl groups in the glycoside link of the polymer and subsequent formation of the amide bond.

The elemental composition of peat lignin after mechanochemical action (see Table 4) provides evidence of clearly pronounced conden-

TABLE 3

Elemental composition of cellulose after cavitation treatment in different aqueous solutions of alkalis

Peat samples	Element, content, %				H/C	N/C	O/C
	C	H	N	O			
Initial	34.19±0.41	4.89±0.04	1.15±0.01	59.77	1.7	0.03	1.3
Treated in NH <sub>4</sub> OH	41.58±0.20	5.79±0.01	2.07±0.08	50.56	1.7	0.04	0.9

TABLE 4

Elemental composition of dioxane lignin after cavitation treatment in different aqueous solutions of alkalis

Peat samples	Element content, %				H/C	N/C	O/C
	C	H	N	O			
Initial	63.77±0.06	8.56±0.47	0.93±0.06	26.74	1.6	$1.2 \cdot 10^{-2}$	0.31
Treated in NH <sub>4</sub> OH	72.50±0.04	10.11±0.00	0.98±0.06	16.46	1.7	$1.2 \cdot 10^{-2}$	0.17
the same, in NaOH	72.67±0.46	10.99±0.07	0.50±0.10	16.84	1.8	$5.9 \cdot 10^{-3}$	0.17
the same, in KOH	71.67±0.50	10.99±0.09	0.50±0.01	16.84	1.8	$6.0 \cdot 10^{-3}$	0.18

TABLE 5

Elemental composition of humic acids after cavitation treatment in different aqueous solutions of alkalis

Peat samples	Element content, %				H/C	N/C	O/C
	C	H	N	O			
Initial	55.41±0.40	5.33±0.08	3.36±0.01	35.90	1.1	$5.2 \cdot 10^{-2}$	0.5
Treated in NH <sub>4</sub> OH	55.14±0.14	6.20±0.02	3.80±0.10	34.51	1.3	$5.9 \cdot 10^{-2}$	0.5
the same, in NaOH	57.76±0.08	6.16±0.07	2.25±0.03	33.83	1.3	$3.3 \cdot 10^{-2}$	0.4
the same, in KOH	57.95±0.28	6.43±0.15	2.00±0.21	33.62	1.3	$2.9 \cdot 10^{-2}$	0.4

sation processes resulting in the destruction of alkyl-aryl ether bonds, while carbon-carbon bonds are formed in their place. The completeness of hydrolysis and accompanying condensation processes is conjugated with the strength of the base used.

One can see in the data on H/C ratios (see Table 4) that the degree of aromaticity of lignin molecules increases, especially with an increase in the strength of the base used for alkaline hydrolysis.

The elemental composition of the resulting HA differs (though insignificantly) from that of HA extracted from the raw material using the standard procedure (see Table 5). They are characterized by the higher carbon content and lower oxygen content.

The use of ammonia as the base naturally leads to an increase in the mass concentration of elemental nitrogen. Quite contrary, the use of stronger bases causes a decrease in its content. The HA obtained as a result of cavitation treatment in the water-ammonia medium is most close in the elemental composition to that of the HA of initial peat. So, the use of the aqueous solution of ammonia is preferable for obtaining HA using this method.

## CONCLUSION

1. Cavitation treatment of peat in alkaline solutions causes structural rearrangement leading to changes in separate fragments of macromolecules, which leads to the formation of the additional amount of humic acids.

2. The most preferable base for obtaining humic acids using this method is the aqueous solution of ammonia.

3. During the cavitation treatment of peat in water-ammonia mixture, nitrogen fixation occurs with the participation of all the components of humate-carbohydrate complex.

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