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# Formation of Humic Acids under Cavitation Impact on Peat in Aqueous Alkaline Media

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## Abstract

The chemical nature of substances formed in aqueous alkaline media in the course of cavitation impact on peat containing no humic acids is considered. Using chemical and physicochemical investigation methods there have been established the nature of humic substances formed. It is proved that the effect of mechanochemical aqueous alkaline medium exerted on humate–carbohydrate complex can result in the formation of humic acids from other components of peat.

**Key words**: humic acids, peat, chemical composition, mechanochemical impact

## INTRODUCTION

Progressive approach to the industrial processing of peat comprises a complex use thereof [1]. Humic acids (HA) are the most valuable and easily extractable components of peat, so the main direction in the processing of peat is associated with obtaining HA therefrom using extraction methods. However, the mentioned production practice does not allow realizing any integrated approach to the use of peat as a valuable raw material. At the same time, methods for producing HA that provide several-fold increasing the practical yield thereof from the peat [2] as well as and obtaining substances, identical with respect to HA from materials not containing them in their structure are known [3, 4]. All these methods are based on the mechanochemical oxidizing action. If the formation of substances such as the HA from lignin-carbohydrate materials is a justified process [5], the extraction of an additional amount of HA from the humate-carbohydrate complex has hitherto not been explained.

The purpose of this work consisted in establishing the nature of the chemical substances that are formed from the solid peat residue (SPR), devoid of HA *via* preliminary extraction.

## EXPERIMENTAL

The authors of [2] demonstrated that the cavitation action of aqueous alkaline media on peat provided the most complete quantitative extraction of HA from peat. It was suggested in the work [6] that chemical processes, identical to the complex biologically driven process of plant residue humification, occurred in peat at the action of such a type. In order to check this hypothesis the SPR produced by the method from [2] being a waste product was separated from the liquid phase, washed with a solution of the appropriate alkali (0.1 mol/L) to yield colourless washing water. Then the SPR was washed with distilled water until obtaining neutral pH and dried to attain constant mass. The SPR obtained in such a way was further used as a raw material.

TABLE 1

Yield of substances obtained *via* aqueous alkaline extraction

| Bases | Yield after cavitation treatment of SPR, % | Yield of HA, % | |
|---|---|---|---|
| | | According to method from [2] | According to method from [8] |
| $NH_3 \cdot H_2O$ | 14.0±0.8 | 51.2±1.2 | – |
| NaOH | 15.4±0.9 | 51.8±3.9 | 19.9±3.1 |
| KOH | 15.1±0.9 | 52.4±2.3 | – |

A weighed portion of SPR was treated with an alkali solution with the concentration of 1 mol/L in a rotary cavitation apparatus designed by Petrakov [7] with the rotation frequency of 3000 $\text{min}^{-1}$ for 10 min; the mixture was then separated by centrifugation. As the alkali we used aqueous solutions of ammonia, NaOH and KOH.

Acidifying the liquid phase with a 10 % sulphuric acid solution up to pH 2 we precipitated the substances under investigation, further the latter were washed with distilled water until the absence of sulphate ion detection, then they were dried to attain constant mass to determine the yield and to examine for the correspondence to the HA. In order to establish the correspondence of the substances obtained to the nature of humic substances, we conducted in parallel an experiment on the isolation of the HA from the feedstock using a standard method [8]. For all the samples obtained, we investigated the elemental composition using a Carlo Erba Strumentazione CHN analyzer, model 1106 (Italy) and registered IR spectra in potassium bromide with the sample mass fraction equal to 1 %. The molecular mass of the compounds obtained was evaluated using a viscometric method [9].

## RESULTS AND DISCUSSION

The data obtained (Table 1) indicate that the additional cavitation treatment of SRP allows to extract substances that are soluble in alkali and insoluble in water.

It follows from Table 2 that the resulting compounds have a similar elemental composition. This fact also confirms the hypothesis of the HA formation in the course of cavitation peat processing. The resulting substances are characterized by a large number of carbon-carbon and carbon-hydrogen bonds, as compared to naturally occurring HA, which due to a decrease in the total amount of oxygen-containing functional groups in the structure thereof.

The analysis of the IR spectroscopic data allows a more detailed understanding of the chemical nature of the substances obtained. It can be seen (Table 3) that they are similar to HA of the natural geneses. Providing the conservation of the ratio of aliphatic and aromatic molecular fragments ($D_{2920}/D_{1610}$) the substances obtained are characterizes by a great number of hydroxyl groups ($D_{3400}/D_{1610}$), carboxyl groups ($D_{1710}/D_{1610}$) and carbonyl groups ($D_{1260}/D_{1610}$) with respect to the total number of aromatic bonds those form the core of the molecule of the substances under consideration. Basing on this, it could be expected that the resulting molecule would have a higher hydrophilicity.

The analysis of molecular masses of the substances obtained shows that research the objects under investigation are polymers. So, the molecular mass of the HA produced according to the technique reported in [8] amounts to (61 400±2250) kg/kmol, that of HA produced

TABLE 2

Elemental composition of substances obtained in NaOH solution

| Samples | Element content, % | | | | H/C | N/C | O/C |
|---|---|---|---|---|---|---|---|
| | C | H | N | O | | | |
| HA obtained according to [8] | 55.41±0.40 | 5.33±0.08 | 3.36±0.01 | 35.90 | 1.1 | $5.2 \cdot 10^{-2}$ | 0.5 |
| HA obtained according to [2] | 57.76±0.08 | 6.16±0.07 | 2.25±0.03 | 33.83 | 1.3 | $3.3 \cdot 10^{-2}$ | 0.4 |
| Substance obtained from SPR | 57.71±0.18 | 6.72±0.01 | 2.09±0.01 | 33.48 | 1.4 | $3.1 \cdot 10^{-2}$ | 0.4 |

TABLE 3

Ratio of the optical density of the absorption bands ($D$) of the IR spectra of substances obtained in NaOH solution

| Objects | $D_{3400}/D_{1610}$ | $D_{1710}/D_{1610}$ | $D_{1260}/D_{1610}$ | $D_{2920}/D_{1610}$ | $D_{1070}/D_{1610}$ |
|---|---|---|---|---|---|
| HA obtained according to [8] | 0.96 | 0.98 | 0.99 | 0.98 | 0.98 |
| HA obtained according to [2] | 0.99 | 0.97 | 0.97 | 1.01 | 0.98 |
| Substance obtained from SPR | 0.99 | 1.04 | 1.07 | 0.92 | – |

as described by the authors of [2] is equal to (105 500±5000) kg/kmol. The substance obtained from the SPR are characterized by the molecular mass equal to (517 000±3260) kg/kmol.

It can be assumed that the high molecular mass of HA obtained using mechanochemical action, is due to the participation of larger (as compared to native HA) “pieces” of lignin–carbohydrate fragments of residual plant cell walls. Owing to a large rate of the mechanochemical process, the peripheral part of the HA is formed from polysaccharides that do not have enough time to became completely hydrolyzed. As a consequence, the HA formed exhibit a great molecular mass at a comparable chemical composition. In favour of this assumption is the fact that the ratio between the aliphatic and aromatic fragments ($D_{2920}/D_{1610}$) of HA molecules produced *via* the technique presented in [2] exhibits a slight increase. The repeated mechanochemical action causes reducing this ratio for the substance obtained from SPR, due to a more profound behaviour of alkali hydrolysis of glycoside bonds. Molecular mass values also indicates the hydrolysis of the peripheral HA parts formed, to all appearance, from polysaccharides.

## CONCLUSION

Basing on the studies performed one can conclude that the mechanochemical impact of aqueous alkaline media on the peat-humate complex results in the formation of polymeric molecules, whose chemical composition is similar to the nature of naturally occurring HA. Herewith, artificially obtained substances of the humic nature are characterized by a substantially higher value of the molecular mass.

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