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## Acid-base properties of modified peat fulvic acid

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### Abstract

The Effect of Mechanochemical modification on the acid-base properties of fulvic acid peat has been studied. It is found that modifying reagent  $\text{CS}(\text{NH}_2)_2$  increases the amount of aromatic fragments and has no effect on the depletion of functional groups.

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### 1. Introduction

It is known that colloidal solid caustobioliths components (soil, peat, brown coal, etc.) define most of their properties such as ion exchange, metabolizing ability and structural composition<sup>1,2</sup>. However, little attention has been paid to issues associated with colloidal state of components of natural high-molecular compounds of humus origin consisting of humic and fulvic acids (FA). At the same time, the question of the existence of individual FA connections is important for further study of FA as natural objects that perform essential ecological functions. It is considered, that FA are in the nature in free state and in the form of complexes with FA, by participating in the formation of colloidal structure. Therefore, the degree of intensity of the FA is determined not only by the absolute content, but the relative amounts of the part that is not related to the humic acids<sup>3-6</sup>.

High molecular carboxylic FA have a higher content of carboxylic and hydroxyl groups involved in metabolic processes compared with humic acids<sup>1,3</sup>. However, the activity of functional groups depending on the FA environment had not previously been studied.

The authors of the works have shown that application of mechano-chemical modification of FA peat causes

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an increase in oxygen-containing groups and strengthens their ability to metabolizing<sup>7</sup>. Therefore, the objective of this work was to evaluate the effect of modifications on the composition and acid-base properties of FA as separate compounds for use in the protection of the environment.

## 2. Experimental part

The objects of research are FA from transitional peat (FA1) is subject to Mechano chemical modification (FA2). As modifying agents NaOH were taken (FA3) and  $\text{CS}(\text{NH}_2)_2$  (FA4). Forsyth held cleanup FA. By  $^1\text{H}$  NMR spectroscopy, an analysis of samples structural transformations on the instrument base of «Tomsk scientific Center hared use of SB RAS» was made. Determination of oxygen-containing groups conducted by potentiometric titration in laboratory ionometre I-160 MI. Determination of the degree of dissociation and the calculation of the dissociation constants of each type groups carried out according to the Henderson-Hasselbach equation.

## 3. Results and discussion

The particular interest is the determination of the effect of mechano-chemical modification of the FA. According to figure 1 it is shown that the modification without reagents significantly contributes to an increase in output in 2 times, and after addition of NaOH and  $\text{CS}(\text{NH}_2)_2$  – almost 3 times. This significant increase in FA after modification due to the destruction of the complexes of humic acids-fulvic acids and release the past.

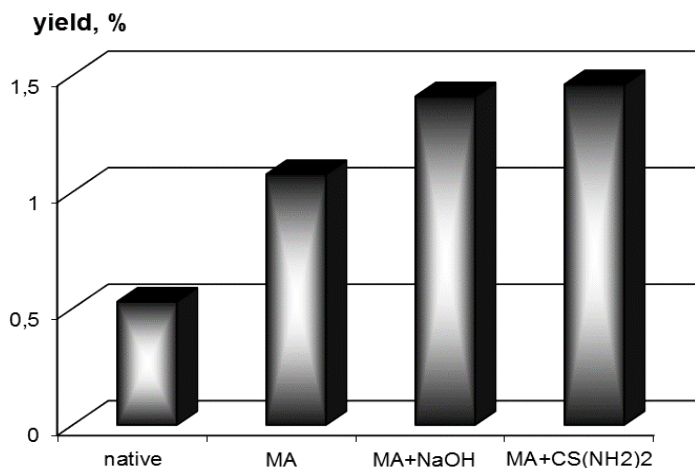


Fig. 1. The effect of Mechano chemical modification to the output of peat fulvic acid

Also considering that the FA are not independent connections but the shards of humic acids, the increase can be explained by the fact Mechano chemical modification process is accompanied by an increase in the surface area of turf peat for extraction and simultaneously destroy associative humic components, as a result of the increasing number of water-soluble "splinters".

For a more detailed study of the influence of modification on structural composition of peat FA was applied NMR method – Spectroscopy (table 1). It is according to the received results, initial sample FA is characterized by several types of hydrogen in almost equal shares. The protons in the  $\alpha$ ,  $\beta$  and  $\gamma$  are the distance from the aromatic nucleus: For-protons,  $\text{CH}$ -,  $\text{CH}_2$ -,  $\text{CH}_3$ -, -connected directly with the aromatic ring; respectively signal a  $\text{H}_\gamma$  remote protons of methyl groups.

After the modification there has been an increase in the proportion of  $\text{H}_{\text{Ar}}$  and  $\text{H}_\alpha$  for among the  $\text{FA4} > \text{FA3} > \text{FA2} > \text{FA1}$ , that reflecting the increasing number of fragments and aromatic substituents on the ring. But reduction of the alkyl chains  $\text{H}_\beta$  almost doubled compared to the original sample that confirms the gap with-with links to the Mechano chemical processing.

Table 1. FA fragment modified composition by  $^1\text{H}$  NMR – spectroscopy.

Sample	$\text{H}_{\text{Ar}}, \text{H-C}\equiv\text{C-}$ 4.9-9.0 ppm	$\text{H}_\alpha, 1.8-3.1$ ppm ( $\text{CH-}, \text{CH}_2\text{-}, \text{CH}_3\text{-}$ )	$\text{H}_\beta, 1.8-1.1$ ppm ( $\text{CH-}, \text{CH}_2\text{-}, \text{CH}_3\text{-}$ )	$\text{H}_\gamma, 1.1-0$ ppm ( $\text{CH-}, \text{CH}_2\text{-}, \text{CH}_3\text{-}$ )
FA1	27.0	24.5	24.5	24.0
FA2	27.5	31.5	22.5	18.5
FA3	32.7	34.6	13.8	18.9
FA4	34.6	35.6	10.2	19.6

Thus, the modification leads to significant changes in the structure of the FA, enriching structure of aromatic components and reducing the share of the alkyl chains.

Analysis of the acid-base properties of FA are shown in table 2, where there is a trend towards an increase in the content of acidic ion groups up to 19 mg-eq/g for FA4, due to maintenance and chemical processes of oxidation with air oxygen.

Table 2. The apparent dissociation constants of acid ionogenic groups modified peat FA.

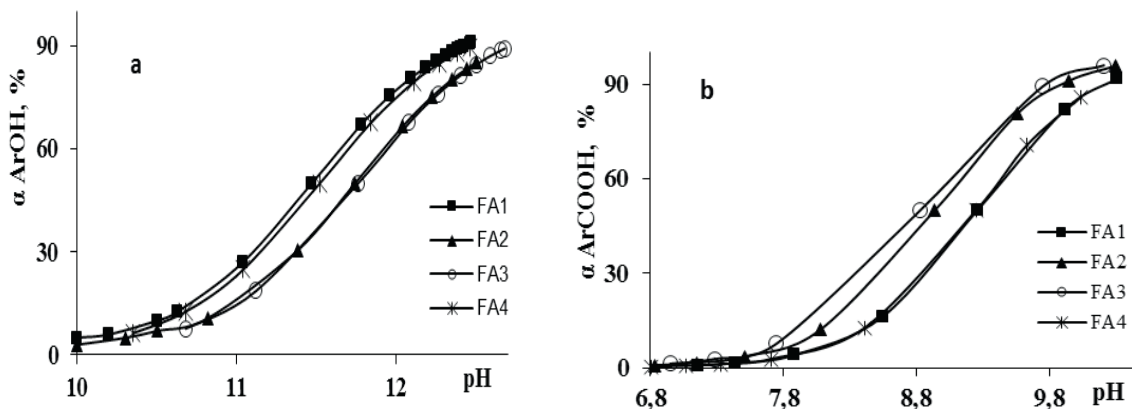
Name of sample	Number of acid ion groups, mg-eq/g	$\text{pK}_{1d} - \text{C}_n\text{COOH}$	$\text{pK}_{2d} - \text{ArCOOH}$	$\text{pK}_{3d} - \text{ArOH}$
FA1	12.6 $\pm$ 0.1*	5.7	9.3	11.5
FA2	15.1 $\pm$ 0.2	5.9	8.9	11.8
FA3	17.8 $\pm$ 0.1	5.6	8.5	11.8
FA4	19.0 $\pm$ 0.3	5.3	9.3	11.5

\* -Confidence Interval,  $P=0.95$ ,  $n=3$

The strength of the acid properties, which can be measured by size, slightly different for groups of  $\text{C}_n\text{COOH}$  and  $\text{ArOH}$ , but increases for  $\text{ArCOOH}$  in structure of FA2 and FA3.

Study of behavior of dissociation of charged groups FA depending on the pH of the environment allows you to determine the effect of Mechano chemical modification and predict the activity of functional groups in different bands in pH.

The results of Figure 2 are consistent with the data obtained by NMR spectroscopy: mechanochemical modification with thiourea has no effect on the nature of the dissociation of functional groups when the aromatic ring ( $\text{ArOH}$ ,  $\text{ArCOOH}$ ). Without modification reagent and NaOH enhances the dissociation the groups under consideration FA 20%.



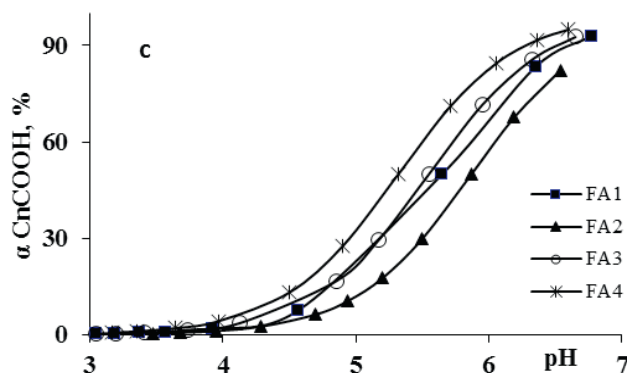


Fig.2. Dissociation of functional groups of peat FA against pH and conditions of modification: a –  $A_rOH$  groups, b –  $A_rCOOH$  groups, c –  $C_nCOOH$  groups

Ionic group  $C_nCOOH$  in FA, dissociating in an acidic environment, exhibits properties most strong acid compared to the others. Referring to Fig. 2, with thiourea modification enhances the properties of the carboxylic acid groups on the ends of the hydrocarbon chain. Modifying without reagents weakens these properties, favoring the formation of ions in the less acidic environment.

#### 4. Conclusion

Thus, peat mechanochemical modification provides increased yield of FA in 2-3 using NaOH and the reactants  $CS(NH_2)_2$ , each of which attaches a particular modification of the structure of a mechanism of an organic substance, that allows to obtain a new set of FA physicochemical properties. Alkaline hydrolysis of peat in the process of mechanical activation has a significant influence on the acid-base properties of the functional groups of aromatic nature FA. Thus modified organic substances become strong detoxifying agents for detoxification of hetero toxic substances.

Also it has been noted that the use of the reagent provides an increase in the proportion of thiourea aromatic component is 7% and the carboxyl groups  $C_nCOOH$ . Such preparation can be recommended for the binding of heavy metals and polycyclic aromatic hydrocarbons.

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