Determination of Humic Acid Content in Sapropel

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Abstract. The agricultural industry, in particular crop farming, is in need of using biological plant and soil protection products, as well as mineral fertilizers. A number of problems associated with soil contamination with substances of chemical nature that are part of mineral fertilizers can be solved through the use of biofertilizers based on humic acids (HA). HA can also be used as plant growth stimulants, restorers of disturbed soils and sorbents of toxic pollutants. One of the promising sources for obtaining HA is sapropel obtained during the reclamation of reservoirs. The study was conducted in order to determine the concentration of humic acids in sapropel harvested in the water bodies of the Republic of Mari El (RME) and to identify the method that assumes the best yield of HA. The object of the study were sapropel samples of various water bodies of the RME. Humic acids were isolated by two methods: the method of alkaline extraction and the method of aqueous extraction. According to the results of the study, significant differences in humic acid concentrations in sapropel samples were noted. It was found that sapropel of the Lake Vodoozerskoye deposit is characterized by the highest content of humic acids. It was also determined that the sapropel of this deposit is the leader in the amount of HA, regardless of the extraction method.

1 Introduction

Sapropel is a substance of predominantly biological origin, which is a silty organogenic sediments of fresh water bodies. Sapropel contains more than 15% of organic substances [1, 2]. Sapropel is formed with low oxygen access from the remains of living organisms as a result of the vital activity of bacteria. Sapropel is quite complex in composition, it consists of: fine particles of mineral and organic origin; macro- and microelements; humic substances; mineral components [3, 4].

The biochemical composition of sapropel mainly depends on the area where it is mined, natural conditions, and the characteristics of the local flora and fauna. Therefore, its composition may vary depending on the deposit. Sapropel contains practically no potassium. It is noted that compared with manure, there is three times less nitrogen and phosphorus in sapropel. The content of organic substances in sapropel is in the range of 12-80%, ash from 20 to 90% in terms of dry matter.

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The organic matter (OM) of sapropels contains: components of mineral nutrition of plants (nitrogen, phosphorus, potassium, calcium, magnesium); trace elements (copper, cobalt, boron, manganese, zinc, iodine, bromine). Since sapropel contains almost all the elements necessary for the normal functioning of plants, when it is introduced into the soil, its agrochemical and water–physical properties improve, as well as crop yields increase [5].

In sapropel, the OM accounts for from 6.7% to 71.2% of humic substances. More than half of humic substances consist of humic acids (HA). HA are mainly neoplasms of lake reservoirs. Mainly humic acids consist of aliphatic structures, but the presence of aromatic fragments in peat sapropels has also been established. HA of sapropel are characterized by an increased content of hydrogen (up to 7.2%) and nitrogen (up to 7%). More than half of the nitrogen of humic acids is represented by amino acids. The concentration of humic acids, as well as their structure, significantly affect the following properties of sapropel: biological activity; biochemical stability; adhesive ability. These properties determine the direction of sapropel use in the national economy.

Sapropel has a positive effect on the yield and quality of cultivated plants, although these observations are mainly applicable only to grain plants [4].

From literary sources, the high efficiency of organo-mineral fertilizer based on sapropel, which includes peat, amorphous silica and mineral fertilizers, was noted. The use of organic-mineral fertilizers based on sapropel has a positive effect on both cultivated plants and the soil substrate as a whole, and not only with direct action, but also in the aftereffect. The authors also note that sapropel acts on plants as a biostimulator of growth. This effect makes it possible to increase crop yields by 40-50% after sapropel is introduced into the soil [6, 7, 8].

Basically, the biological activity of sapropel is caused by the presence of humic acids in it. Humic acids are one of the main components of humus and humic substances. HA improve the chemical and physical quality of the soil.

Humic acids are soluble in alkalis and insoluble in acids (at pH < 2). Their salts are called humates. With monovalent cations (K^+, Na^+, NH^{4+}), HA form water-soluble salts, and with divalent and trivalent cations (Ca^{2+}, Mg^{2+}, Al^{3+}, Fe^{3+}) they easily precipitate [9].

2 Materials and Research Methods

In this work, sapropel samples from various water bodies of the Republic of Mari El were used, collected in the field in the spring - summer period of 2021.

Samples of sapropel taken from the deposits: "Lake Tabashino", "Lake Posyar", "Lake Vodoozerskoe" of the Republic of Mari El were used as objects of research.

Description of deposits:

- "Lake Tabashino" in the Orsha district. It is a karst lake located in the north of the Yoshkar-Ola watershed plain area of mixed forests, in the interfluve of Bolshaya Kokshaga and Malaya Kokshaga. Parameters of this lake: depth - 53 meters; area - 26 hectares. The lake has a rounded-oval shape. The bottom of the lake is muddy. The water is clear, fresh. Sandy-clay deposits lie in the vicinity. The lake is fed by the Pyzhanka River [10, 11].

- "Lake Posyar" in the Kilemarsky district. This lake is located in the vicinity of the settlement - the village of Kuplonga. Geographically, the lake is located on the right bank of the Bolshoy Kundysh River. The lake has a rounded shape. Its area is 78 hectares. The water in the lake is yellowish. By natural origin, sapropel, which lies in this lake, is of a limonite species. Sapropel of this deposit can be recommended for the production of fertilizers, with the exception of limonite sapropel species [12, 10].

- "Lake Vodoozerskoe" in the Kilemarsky district. This water body is located one kilometer from the village of Kilemary. The geographical location is noted in the left-bank floodplain of the Bolshoy Kundysh River. Its area is 51 hectares. Industrial production of

sapropel, a valuable organic fertilizer, is carried out on the lake. Sapropel of this deposit was assigned to the organic class [13].

Sapropel samples were dried to complete dehydration at a temperature of 105 °C. Further, the samples were crushed before passing through a sieve with a mesh size of 0.2 mm.

The schemes of alkaline and aqueous extraction of humic acids are described in detail in [14, 15], respectively.

Quantitative determination of humic acid content was carried out by spectrophotometry. To construct the calibration graph, standard solutions of humic acids were prepared in increments of 1 g/l. UV absorption spectra of HA extracts were recorded using instrumental methods. The optical densities of the solutions were taken on a SmartSpec ^{tm} Plus spectrophotometer at a wavelength of 350 nm in a quartz cuvette with a thickness of 10 mm. The following comparison solutions were used: 1% sodium hydroxide solution and distilled water for alkaline and aqueous extracts, respectively [16].

3 Results and Discussion

To construct a calibration graph, measurements of the optical density of standard HA solutions were carried out. The concentration of solutions was:1 g/l, 2 g/l, 3 g/l, 4 g/l, 5 g/l, 6 g/l, 7 g/l, 8 g/l, 9 g/l, 10 g/l. To obtain solutions of these concentrations, dry humic acid powder was dissolved in a 1% solution of sodium hydroxide (NaOH). Measurements of the optical density of standard solutions are presented in Table 1.

Table 1. Optical density indicators of standard solutions

Concentration (g/l)	1	2	3	4	5	6	7	8	9	10
Optical density of HA (λ350)	0.295	0.535	0.723	1.043	1.230	1.581	1.783	1.906	2.398	2.676

Based on the data obtained (Table 1), a calibration graph was constructed (Figure 1).

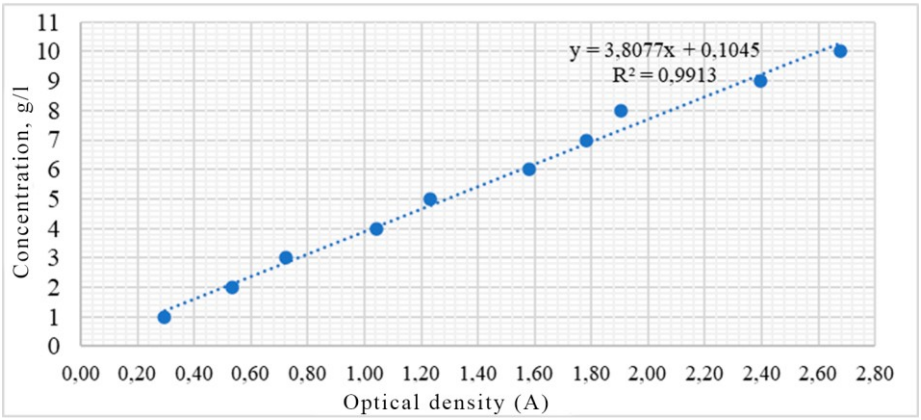

Fig. 1. Calibration graph

For further research, it was necessary to carry out alkaline extraction of humic acids. The optical density was measured in the obtained extracts.

According to the values of optical densities obtained during spectrophotometric analysis, as well as using the calibration graph and the regression equation obtained during

its construction, the quantitative content of humic acids in extracts isolated from sapropel from various deposits was determined.

Next, the concentrations of HA in extracts isolated according to GOST 9517-94 (ISO 5073-85) "Solid fuel. Methods for determining the yield of humic acids" from sapropels of various deposits (Table 2).

Table 2. Concentration of HA in extracts isolated according to GOST 9517-94

Deposit	Concentration of HA, g/l
"Lake Tabashino"	2.713 ± 0.0127
"Lake Posyar"	3.487 ± 0.0346
"Lake Vodoozerskoe"	3.662 ± 0.0184

Thus, it was found that by the presence of humic acids (3.662 ± 0.0184 g/l), sapropel obtained from the Lake Vodoozerskoye deposit is in the lead. Sapropel of the Lake Tabashino deposit, according to the results of the analysis, contains the smallest amount of humic acids (2.713 ± 0.0127 g/l).

Water extraction of humic acids from sapropel was also performed. After analyzing the data obtained, the concentrations of HA were determined in extracts isolated according to GOST R 54221-2010 "Humic preparations from brown and oxidized coal. Test methods". The quantitative content of HA in extracts is presented in Table 3.

Table 3. Concentration of HA in extracts isolated according to GOST R 54221-2010

Deposit	Concentration of HA, g/l
"Lake Tabashino"	1.456 ± 0.0582
"Lake Posyar"	1.704 ± 0.0112
"Lake Vodoozerskoe"	2.336 ± 0.0293

As a result of the study, it was found that the largest amount of HA (2.336 ± 0.0293 g/l) is contained in sapropel samples obtained from the Lake Vodoozerskoye deposit. The lowest yield of humic acids (1.456 ± 0.0582 g/l) is characterized by sapropel of the Lake Tabashino deposit.

Table 4 presents the data of a comparative analysis of the humic acid content depending on the sapropel deposit and methods for obtaining extracts.

Table 4. Concentration of HA in extracts

Deposit	Method I	Method II
	Concentration of HA, g/l	Concentration of HA, g/l
"Lake Tabashino"	2.713 ± 0.0127	1.456 ± 0.0582
"Lake Posyar"	3.487 ± 0.0346	1.704 ± 0.0112
"Lake Vodoozerskoe"	3.662 ± 0.0184	2.336 ± 0.0293

Note: Method I — GOST 9517-94 (ISO 5073-85). The solid fuel. Methods for determining the yield of humic acids; method II – GOST R 54221-2010. Humic preparations from brown and oxidized coal. Test methods.

4 Conclusions

During the study, extracts of humic acids were isolated from sapropel from various deposits of the Republic of Mari El. The quantitative content of humic acids was determined by spectrophotometry.

It was noted that extracts obtained from sapropel from the Lake Vodoozerskoye deposit are leading in terms of humic acid content. At the same time, it was determined that the

sapropel of this deposit is the leader in the concentration of HA, regardless of the extraction method.

Also, according to the results of the study, it was noted that when using the method I – GOST 9517-94 (ISO 5073-85) "Solid fuel. Methods for determining the yield of humic acids" the best yield of humic acids is achieved. At the same time, the yield of HA from extracts obtained by this method exceeds the yield of HA when using method II – GOST R 54221-2010 "Humic preparations from brown and oxidized coal. Test methods" almost 2 times.

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