Artículo de investigación

The study of the chemical composition of humic acids of initial and heat-treated sapropels of lakes of the Surgut district of the Khanty-Mansi autonomous Okrug – Yugra

El estudio de la composición química de los ácidos humicos de los sapropels iniciales y tratados con calor de los lagos del distrito de Surgut del Khanty-Mansi autonomo Okrug – Yugra

O estudo da composição química dos ácidos húmicos dos sapropels iniciais e tratados termicamente dos lagos do distrito de Surgut da autónoma Khanty-Mansi Okrug – Yugra

Recibido: 20 de septiembre de 2018. Aceptado: 11 de octubre de 2018

Written by:
Sartakov M.P. (Corresponding Author)[13]
Chumak V. A.[14]
Grekhova I.V.[15]
Efanov M.V.[16]

Abstract

This article shows the effect of heat treatment of sapropels on the changes in the chemical composition of humic acids derived from them. Data on changes in the content of elements, the atomic relations, the degree of oxidation, graphic and statistical feature have been presented. The effect of heat treatment from 150 to 2500C on the dynamics of the processes of decarboxylized and dehydration, a comparison of the results obtained of elemental composition of humic acids of initial and heat-treated sapropels.

Keywords: Humic acids, Surgut lakes, sapropel, Khanty-Mansi Autonomous Okrug – Yugra, elemental composition.

Resumen

Este artículo muestra el efecto del tratamiento térmico de los sapropeles sobre los cambios en la composición química de los ácidos húmicos derivados de ellos. Se han presentado datos sobre cambios en el contenido de los elementos, las relaciones atómicas, el grado de oxidación, la característica gráfica y estadística. El efecto del tratamiento térmico de 150 a 2500C sobre la dinámica de los procesos de descarboxilación y deshidratación, una comparación de los resultados obtenidos de la composición elemental de ácidos húmicos de sapropeles iniciales y tratados térmicamente.

Palabras claves: Ácidos húmicos, lagos Surgut, sapropel, Okrug autónomo de Khanty-Mansi - Yugra, composición elemental.

Resumo

Este artigo mostra o efeito do tratamento térmico de sapropels sobre as alterações na composição química dos ácidos húmicos derivados deles. Dados sobre mudanças no conteúdo dos elementos, as relações atômicas, o grau de oxidação, a característica gráfica e estatística foram apresentados. O efeito do tratamento térmico de 150 a 2500C na dinâmica dos processos de descarboxilização e desidratação, uma

[13] Yugra State University, Chekhov 16, Russia
[14] State Agricultural University of Northern Zauralie, 7 Republics st., Tyumen, Russia
[15] LLC "Small Innovative Company Yugra-Biotechnology", Student, 27, Khanty-Mansiysk, Russia
[16] LLC "Small Innovative Company Yugra-Biotechnology", Student, 27, Khanty-Mansiysk, Russia

comparação dos resultados obtidos da composição elementar de ácidos húmicos de sapropels iniciais e tratados termicamente.

Palavras-chave: ácidos húmicos, lagos Surgut, sapropel, Okrug Autônomo de Khanty-Mansi - Yugra, composição elementar.

Introduction

Humic acids are widely spread in nature. They are part of soil, peat and sapropels. The chemical nature of this group of organic compounds is considered to be inadequate. Possessing a number of useful properties, the need to investigate their physical and chemical characteristics, which determine their practical application in various spheres of life, increases (Komissarov and Loginov, 1971).

It is necessary to determine chemical composition and molecular structure of the humic acids from different raw materials to deliberately apply them (Savchenko et al, 2006).

Currently, humic acids have a wide range of applications. Most often they are used as plant stimulant fertilizer in agriculture, as well as in the remediation of contaminated soils and waters. As surface-active substances, humic acids are used as components of boracic and cement slurry solutions. Treatment research of cancer is actively conducted on the basis of humic acids of sapropels in medicine. Sapropels are sediments of freshwater bodies formed from dead remains of plants and living organisms.

There are numerous data on humic acids extracted from peat and coals, which cannot be said about the sapropels: their physical and chemical aspects are understudied. Sapropels have not been studied in Khanty-Mansi Autonomous Okrug-Yugra. In this regard, there is a need in research of humic acids of sapropel physical and chemical properties for the production of drugs based on them.

At present, HA are widely used in cosmetics and mudtherapy, as dietary supplements, since they can adsorb xenobiotics and antigens, derivatives of humic acids can be used as redox -, and complexing agents. Humic acids are used for the rehabilitation of contaminated lands in the petroleum industry.

.

Subjects and Research Method

We have studied humic acids of lakes of the basin of the Ob river, its right bank (Surgut lakes). All the lakes are fresh in the composition of the ions, many lakes do not have names.

Samples were taken from bottom sediments of lakes Bezymyannoye No. 1, Bezymyannoye No. 2 and Bezymyannoye No. 3 in a distance of 5 m from the coastal edge at a depth of 1.5 m.

Samples of the original sapropels were thermo processed in a simple way, for this reason sapropels were milled in a mortar, then a thin layer of 1 mm were placed on a metalpaper, after which the envelope was formed. Small cross-shaped incision was made in the middle of the envelope, approximately in 1cm so that thermal decomposition of humic acids was carried out in the private environment of gases of decomposition during the heat treatment, only a couple of adsorptive water were removed through a hole. Heat treatment of the obtained samples of sapropels was performed in a muffle furnace at 150°C, 200°C, 250°C.

Revealing of carbon, hydrogen and nitrogen-12 samples of humic acids of initial and heat treated sapropels in Khanty-Mansi Autonomous okrug was carried out in elemental analyzer Euro Vector EA 3000 m+od.

Results and Discussion

Elemental composition of humic acids of initial and heat treated sapropels differs and changes within certain limits, as shown in table 1. The carbon content ranges from 29.6 per cent to 51.8%, hydrogen from 3.7% to 4.6%, nitrogen from 2.1% to 3.3%, oxygen and sulphur content was calculated with the standard method by difference, where the oxygen content ranges from 37,9% to 62.4%, and the percentage of sulphur is only 1-2%

Table 1 – Elemental composition of humic acids of initial and heat treated sapropels on ash-free substance.

Sample	Heat treatment 0C	Weighed quantity, mg	C%	H%	N%	O+S%	Ash content in %
Lake	----	1,1935	41,5	3,9	2,1	52,6	15,5
Bezymyannoye	150	1,1155	48,7	4,4	2,3	44,6	15,5
№1	200	1,2345	51,3	4,6	2,7	41,5	15,5
	250	1,3485	53,8	4,1	3,3	38,9	15,5
Lake	----	0.8770	29,6	3,7	2,4	64,4	18,2
Bezymyannoye	150	1,1048	43,5	3,6	2,3	50,6	18,2
№2	200	1,0280	51,3	4,6	3,4	40,7	18,2
	250	0,8595	51,8	4,3	3,1	40,9	18,2
Lake Bezymyannoye №3	----	0,6125	38,5	3,7	2,6	55,2	23,9
	150	0,5630	40,6	4,0	3,2	52,3	23,9
	200	0,8180	40,6	3,9	2,8	52,7	23,9
	250	1,1690	49,2	4,0	2,1	44,8	23,9

The results of the elemental analysis allowed to characterize some features of humic acids of different Surgut lakes and gave information about the principles of their structure. It is best to use not percentage composition of humic acid, discovered in the analysis, but atomic ratio of elements compounding a simple formula and applying the principles of graphical and statistical analysis (table.2).

Atomic ratio N:C, O:C, N:C, as known, show the number of atoms of hydrogen, nitrogen and oxygen, which substances of one carbon atom contain in the molecule (particle) of humic acid. The smaller the relationship, the greater role carbon atoms play in the composition of molecular structures. The decrease in the atomic relations indicates the increasing share of benzenoid components and the decreasing in the proportion of aliphatic side chains in the molecules of humic acids. The relative branching of the side chains, degree of oxidation, the role of nitrogen-containing compounds in the formation of humic acids were judged by the ratio in each of the pairs (Sartakov et al, 2015; Sartakov et al, 2017).

Table 2- atomic ratio, the degree of benzenoid (α) and the heat of combustion of humic acids.

Sample	**Thermal treatment 0C**	**H/C**	**O/C**	**N/C**	**C aliph.**	**α, %**	**Q, kJ/kg**
	---	1,12	0,95	16,94	0,65	35	13251
Lake Bezymyannoye	150 °C	1,07	0,69	18,15	0,61	39	17188
№1	200 °C	1,07	0,61	16,29	0,60	40	18659
	250 °C	0,91	0,54	13,98	0,55	45	19161
	----	1,49	1,63	10,42	0,74	26	7676
Lake Bezymyannoye	150 °C	0,98	0,87	16,21	0,61	39	13766
№2	200 °C	1,07	0,60	12,93	0,60	40	18746
	250 °C	0,99	0,59	14,32	0,58	42	18517

Lake Bezymyannoye № 3	----	1,14	1,09	12,69	0,66	34	11641
	150 °C	1,17	0,97	10,87	0,66	34	13097
	200 °C	1,14	0,97	12,43	0,65	35	12931
	250 °C	0,97	0,68	20,08	0,59	41	16833

The lowest ratio (H/C) is typical for the lake Bezymyannoye No. 1, at heat treatment 250°C (0,91), and lake Bezymyannoye No. 3, at heat treatment 250 °C (0.97) and the lake Bezymyannoe No. 2 heat treatment at 150-250 °C (0,98-0,99) also they have the highest degree of benzenoid content (45%, 41% and 40%). Humic acids extracted from the not heat-treated sapropels are characterized by the lowest values of the degree of benzenoid content (26%, 34% and 35%).

Low degree of humification may be confirmed not only by the results of the chemical composition, pointing at the high content of aliphatic fragments, but the data of the nuclear magnetic resonance and electron paramagnetic resonance. (Chukov et al, 2017; Chukov, 2017).

HA molecule is stronger subjected to modification when increasing treatment temperature from 150 to 250, reduces the percentage of compounds without aroma bonds, and stable nuclear part remains almost unchanged, the main properties of macromolecules are preserved (paramagnetic activity) (Chukhareva et al, 2016; Chukhareva et al, 2015).

According to previous studies, a higher processing temperature 300 negatively affects the structure of humic acids, nuclear part already begins to break down and the condensation of macromolecule core interferes (Chukhareva et al, 2003).

An atomic ratio of H:C is an important criterion according to Van-Krevelen, which clearly characterizes the class of hydrocarbons. That ratio is typically approximately equal to 1.0 for humic acids of sapropels, which formally indicates the predominance of aromatic structures. Accurate interpretation of HA through graphical and statistical analysis is complicated by the fact that there is no complete information about the oxygen function in the molecule and the number of carbon atoms per molecule (Sartakov et al, 2017).
Evaluation of atomic relations allows solving some of the issues of the mechanisms of transformation of plant residues, and certain groups of humic substances. For this purpose it is convenient to use the chart of atomic relations H:C-O:C which presents the results of the analysis of the elemental composition of HA of the studied peat (Orlov, 1970).

Relationship H:C varies in the range from 0,97 (HA of heat-treated sapropels up to 250 °C) to 1.49 (HA of not heat-treated samples of sapropels). The average value of H:C of humic acids of sapropels of lakes of Khanty-Mansi Autonomous Okrug-Yugra (12 samples) amounts 1.09.

Figure 1 shows the diagram of Van Krevelen. All the samples on it were distributed to three areas. The diagram shows that decarboxylation occurs during the transition from area III to area I (or rather, the loss of atoms C and O in the ratio 1:2) and dehydration (loss of atoms H and O in the ratio 2:1). The differences between those areas are more associated with the difference in the number of oxygen atoms, and the relationship H:C in all three regions is more homogeneous.

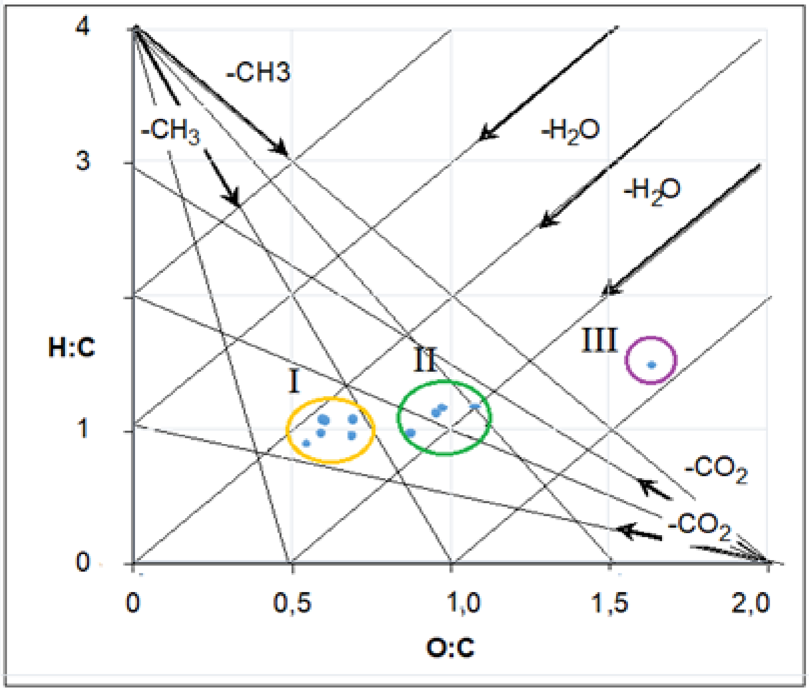

Figure 1 – Generalized diagram of atomic relations H:C-O:C of sapropels humic acids.

Some deviations of the sequence of arrangement of humic acids by the degree of benzenoid content taking into account the relations O:C may be due to the presence of sulfur, and the found value of O by the difference may not be sufficiently reliable.

Most of the samples are located in the first area, where there are the most "mature" humic acids. The largest proportion of aromatic structures corresponds to them, which is confirmed by the lowest values of ratios H:C.

We analyze the 1st area of the different groups of humic acids, which is the most symptomatic, as it contains the ground mass of humic acids (6 of 12) insufficient reliability of the results in oxygen affects less in this area.

The average atomic ratio values of humic acids of the 1st group:

1) Lake Bezymyannoye №1: heat treated up to 200°C, 250°C (2 samples) – H:C = 0,99, , O:C=0,58;
2) Lake Bezymyannoye №2: heat treated up to 150°C, 200°C, 250 °C (3 samples) – H:C = 1,01, O:C=0,67;
3) Lake Bezymyannoye №3: heat treated up to 250 °C (1 sample)– H:C = 0,97, , O:C=0,68.

We analyze the 2nd area of different groups of humic acids, which is less symptomatic, since it has not a large amount of humic acids (5 samples of 12) and not enough reliable information on oxygen effects it:

1) Lake Bezymyannoye №1: heat treated up to 150 °C and the initial (2 samples) – H:C = 1,1, O:C=0,78;
2) Lake Bezymyannoye №3: heat treated up to 1500C, 200 °C and the initial (3 samples) – H:C = 1,15, O:C=1,01.

We analyze the 3rd area of the different groups of humic acids, in which the amount of humic acids is only one from 12 samples, and it is the farthest point and the most decarboxylized. From this we can conclude that this macromolecule of HA is the most unformed and it has more aliphatic fragments:

1) Lake Bezymyannoye №2 (1 initial sample) – H:C = 1,49, O: C=1,63.

From the obtained data it is clear that the structure of the macromolecule of HA has modified stronger with heat treatment in lake Bezymyannoye No. 2, which is evidenced by the values of atomic relations in comparison with the initial sample. HA of lake Soviet, were subjected to thermal modification too, but not so much as in lake Bezymyannoye.

Additionally, it should be noted that the degree of oxidation (D.S. Orlov, 1970) is a very useful criterion for identifying the specificity of the transformation of organic matter in different conditions. The oxidizing modifications predominate in redox processes in HA of sapropels and have a positive value (table.3)

Table 3 – Elemental composition (atomic %) and the degree of oxidation (ω) of humic acids of sapropels

Sample	Heat treatment 0C	C,%	H,%	N,%	O+S,%	ω
Lake Bezymyannoye №1	-----	32,1	35,9	1,4	30,6	0,8
	150 °C	35,7	38,3	1,4	24,5	0,3
	200 °C	36,8	39,2	1,6	22,3	0,1
	250 °C	40,0	36,2	2,1	21,7	0,2
Lake Bezymyannoye №2	-----	23,9	35,5	1,7	39,0	1,8
	150 °C	34,5	33,9	1,6	30,1	0,8
	200 °C	36,8	39,2	2,1	21,9	0,1
	250 °C	38,0	37,5	1,9	22,5	0,2
Lake Bezymyannoye №3	-----	30,4	34,8	1,8	33,0	1,0
	150 °C	31,2	36,5	2,1	30,2	0,8
	200 °C	31,5	36,0	1,8	30,7	0,8
	250 °C	37,2	36,0	1,4	25,4	0,4

The values of atomic ratios very differ from the percentages when comparing pairs of elements with dramatically different atomic masses (C-H, O-H). Interest and atomic relations are sometimes almost identical with close atomic masses.

Conflict of Interest

The author confirms that the submitted data does not contain conflict of interest.

Acknowlrdgement

The work was carried out with the financial support of the Russian Foundation for basic research (Contract No. 18-44-860010\18) and the government of the Khanty-Mansi Autonomous Okrug–Yugra (Contract No. 7/18.0392/05.5/18-ЮГУ-124).

Deductions

1) It has been shown using the example of lakes of sapropels of Surgut region with different degree of mineralization, that thermal stability of humic acids increases as a result of preliminary heat treatment of sapropels. This is evident in the ratio of elements.
2) The dependence of the influence of preliminary heat treatment of sapropel from chemical composition of the extracted humic acids. The most stable preparations have been obtained from heat-treated sapropels to 250 °C. Heat treatment from 150 up to 200 °C contributes to a less extent of modifications of macromolecules.

Reference

Chukhareva, N. V., Maslov, S. G., & Sartakov, M. P. (2015). Modification of peat humic acids. Research Journal of Pharmaceutical, Biological and Chemical Sciences, 6(6), 1516-1524.

Chukhareva, N. V., Sartakov, M., & Korotchenko, T. V. (2016). Alteration in elemental and functional composition of heated peat humic acids. In MATEC Web of Conferences. Chemistry and Chemical Technology in XXI Century. Les Ulis. 85, 1004. EDP Sciences.

Chukhareva, N. V., Shishmina, L. V., & Novikov, A. A. (2003). Kinetics of thermal degradation of humic acids. Khimiya Tverdodo Topliva. (6), 37-48.

Chukov, S. N., Ekhar'ko, E., & Abakumov, E. V. (2017). Features of humic acids of soils in the tundra zone in the North of Western Siberia by spectroscopy of electron paramagnetic resonance [Text]. Soil Science. 1, 35–39.

Chukov, S. N., Ejarque, E., & Abakumov, E. V. (2017). Characterization of humic acids from tundra soils of northern Western Siberia by electron paramagnetic resonance spectroscopy. Eurasian Soil Science. 50 (1), 30-33.

Komissarov, I. D., & Loginov, L. F. (1971). Humic preparations. Proceedings of the Tyumen agricultural Institute. 14, 266.

Orlov, D. S. (1970). Element composition and the degree of oxidation of humic acids. Biologicheskie Nauki, 1, 5-20.

Sartakov, M. P., Shpynova, N. V. Deryabina, Yu. M., & Komissarov, I. D. (2015). Elemental composition of humic acids of sapropels of the Middle Ob region and the south of Ob-Irtysh basin, Western Siberia. Chemistry in the interest of sustainable development. 23(5), 523-526.

Sartakov, M. P., Chukhareva, N. V., & Korotchenko, T. V. (2017). Physico-chemical properties of peat humic acids (Middle taiga of western Siberia). International Multidisciplinary Scientific GeoConference Surveying Geology and Mining Ecology Management, SGEM. 421-428.

Savchenko, I. A. Plaksin, G. V., & Krivonos, O. I. (2006). Analyzing products of thermal processing of sapropels of Omsk region. Omsk scientific Bulletin. Series: Land Resources. Humanity. – Omsk. 168-174.