ЕҢБЕК ҚЫЗЫЛ ТУ ОРДЕНДІ
«Ә. Б. БЕКТҰРОВ АТЫНДАҒЫ
ХИМИЯ ҒЫЛЫМДАРЫ ИНСТИТУТЫ»
АКЦИОНЕРЛІК ҚОҒАМЫ

ҚАЗАҚСТАННЫҢ ХИМИЯ ЖУРНАЛЫ

ХИМИЧЕСКИЙ ЖУРНАЛ КАЗАХСТАНА

CHEMICAL JOURNAL of KAZAKHSTAN

АКЦИОНЕРНОЕ ОБЩЕСТВО
ОРДЕНА ТРУДОВОГО КРАСНОГО ЗНАМЕНИ
«ИНСТИТУТ ХИМИЧЕСКИХ НАУК
им. А. Б. БЕКТУРОВА»

3 (67)

ИЮЛЬ – СЕНТЯБРЬ 2019 г.

ИЗДАЕТСЯ С ОКТЯБРЯ 2003 ГОДА

ВЫХОДИТ 4 РАЗА В ГОД

АЛМАТЫ
2019

UDC 541.128

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METHOD OF PRODUCING HUMIC SUBSTANCES FROM LOW-MINERALIZED SULFIDE SILT MUDS (PELOIDS)

Abstract. In **t**his paper is describes a method of producing humic substances from Saki low-mineralized sulfide silt mud. It is shown that the yield of humic substances from therapeutic muds using this method reaches 6-6.5%. Also the initial peloid and humic substances isolated from it were investigated by IR spectroscopic analysis. The nature of the functional groups of substances were determined by the number and position of the peaks in the IR absorption spectra. The suggested method of producing humic products from low-mineralized sulfide silt muds (peloids) makes it possible to obtain purified, therapeutically highly effective, ecologically-economically advantageous products for physical therapy in the conditions of resorts.

Key words: sulfide silt muds, peloid, humic substances, fulvic acids, hymatomelanic acids, method for producing, Saki deposit.

Introduction. Pelotherapy or mud therapy is one of the most ancient methods of treatment by natural factors, which have the greatest adaptogenic potential, being habitual stimuli, have a pronounced training effect [1, 2].

Pelotherapy can be considered a universal method of healing the body, since the range of diseases for which a positive effect is observed is quite wide [3]. Therapeutic muds have an immunomodulatory effect, causing natural adaptive responses of the human body [4, 5], has anti-inflammatory, desensitizing, antitumor [2, 6, 7], analgesic and resorptional action [8], improve hemodynamics and lymphodynamics, reduce the activity of both exudative and infiltrative processes, and soften the adhesive structures [9]. Mud therapy is successfully used in the treatment of various pathologies; in arthritis, respiratory diseases, dermatological diseases, gastrointestinal diseases, gynecological disorders, ulcus cruris, hepatitis, inflammatory respiratory diseases, periodontium [10].

The therapeutic effects of mud are due to the combination of the effect of closely related thermal, mechanical, chemical and biological factors. Depending on the physico-chemical composition of muds, the severity of the biological responses of each of them is different. The literature describes studies concentrated on the study of the composition of therapeutic muds, but they all characterize the mineral component of mud, and almost do not discuss the functional ability of the organic component. The lack of knowledge of the organic substances of therapeutic muds caused their underestimation in the mechanism of action on the body [11].

If several years ago humic substances were used mainly in agriculture and animal husbandry, today their use has proven to be highly-demanded in phar-

macy. The study of their physico-chemical and pharmacological properties will improve the effectiveness and accessibility of pelotherapy for patients, make treatment dosed. Peloid products are easier packed and transported; they do not require special conditions for their storage. In the mud baths, waste material (mud) is disposed of, although valuable substances are stored in it. The active components isolated from these "wastes" can later be used to isolate humic substances and produce peloid products.

The Kazakhstan market of medicines is full of antioxidants of foreign origin, which affects their final price paid by the consumer. The country needs domestic products which can make a worthy competition. Thus, research on the creation of innovative products based on humic substances, peloids, is of particular importance and relevance.

EXPERIMENTAL PROCEDURE

In this regard, we investigated the isolation of humic substances of low-mineralized sulfide silt muds of the Saki Lake by the method [7, 9].

The Saki mud deposit is located in the Saki District of the Republic of Crimea, 45 km north-west of the city of Simferopol and 20 km east of the city of Yevpatoria. The deposit is a coastal, drainless one, with an artificially regulated hydrological and hydrochemical regime. Balance reserves of therapeutic muds are as follows: in the East (Resort) basin there are 986,000 m^3 and in the West (Factory) basin 3,735 m^3.

Externally, mud looks like a homogeneous high-plastic mass of dark gray color, with black interlayers, with the smell of hydrogen sulfide and with a small sediment of the liquid phase.

Humidity of dirt is low – 38.14%, volume weight – 1.73 g/cm^3, shear resistance is 1,973 dyn/cm^2 at the rate of 1,500-1,400 dyn/cm^2. The heat capacity, depending on the magnitude of humidity, is small 0.51 cal/g-grad, the reaction of environment is neutral (pH – 7.45), and the oxidation-reduction potential is negative (Eh – 180 mV). The hydrophilic colloidal complex in its value (22.27% of dry matter) turned out to be slightly less compared to the usual one for natural Saki mud (25%). Impurity of mineral particles with a size of 0.25-5.0 m is 2.5% with the rate of no more than 3%; mineral inclusions larger than 5 mm are absent. Balneologically valuable components were found in mud: organic substances – 3.28% on dry matter; iron sulfides – 0.69% on dry matter; salinity of the mud solution refers to the category of the salt-saturated type – 187.505 g/dm^3; boric acid – 0.115 g/dm^3, which corresponds to the conditional performance. Heavy metals are contained in small quantities, including the most toxic ones – lead, cadmium, zinc and copper.

RESULTS AND DISCUSSIONS

In order to destruct mineral complexes and remove sulfides, carbonates and other mineral components, native mud was treated with a 2M solution of hydrochloric acid without thermal exposure in order to prevent the destruction of organic substances (figure 1).

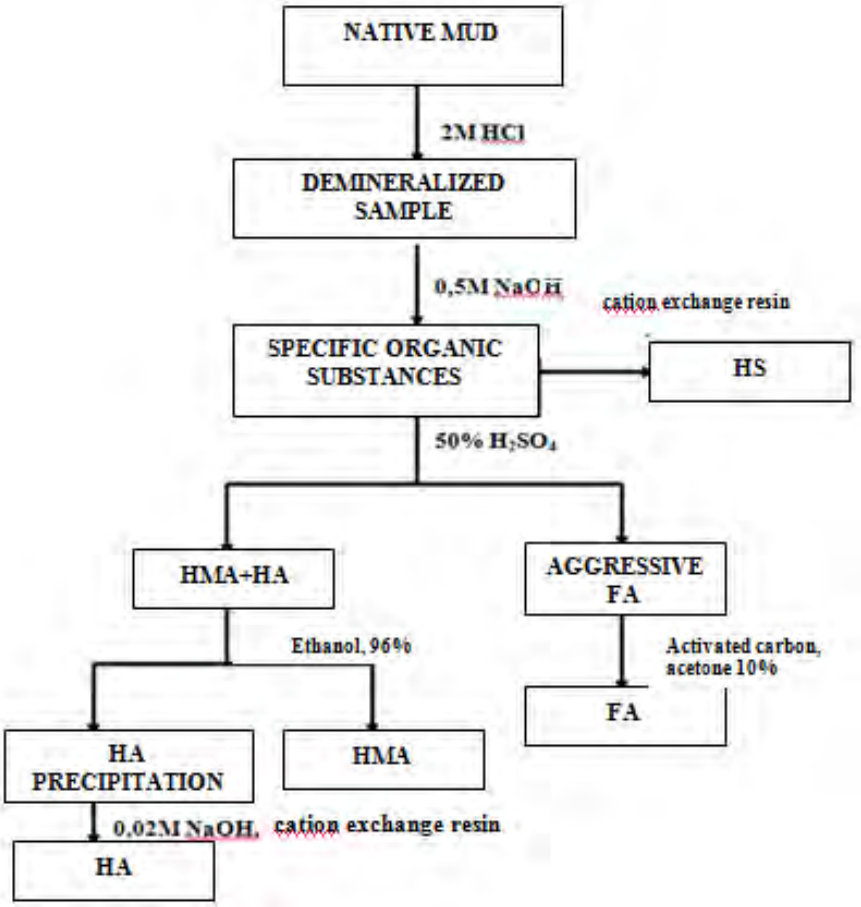


Figure 1 – Scheme of isolation of humic substances of low-mineralized sulfide silt muds: HA – humic acids, FA – fulvic acids, HMA – hymatomelanic acids, HS – humus substances (acids)

In order to obtain more pure products, the extraction of specific organic substances was carried out with a 0.5 M solution of sodium hydroxide in peloid – solvent ratio of 1:10 no more than three times, since in subsequent portions the amount of mineral components increases significantly.

At this stage, the extract containing the amount of fulvic, hymatomelanic and humic acids – humus acids was obtained. In order to obtain this product, we abandoned the salt additives provided by the method of D.S Orlov. The extract, which represents a mixture of sodium salts of humus acids, was transferred to the H-form, passing through a cation exchange resin. The product was brought to the air-dry state at a temperature of 35-40°C using forced ventilation.

For further fractionation of specific organic substances, the precipitate was filtered and a 50% solution of sulfuric acid was added to the filter to pH = 1.0 (universal indicator). The liquid from the precipitate was decanted, filtered and

transferred to the adsorbed state on activated carbon, after which they were purified by the method of Forsyth (Forsyth W.G.L., 1947). A fraction was removed from the coal with a solution of 0.5 M sodium hydroxide solution and transferred to the H-form using a cation exchange resin, controlling the constancy of pH on the ionomer. The product was dried at a temperature not exceeding 35°C. At this stage a fraction of fulvic acids was obtained.

The residue on the filter after separation of the fulvic acid fraction was washed with water until a negative reaction to sulfate ions and exhaustive extraction with ethanol was carried out until pale yellow color of the extractant (fraction of hymatomelanic acids). After vacuum distillation of the maximum possible amount of solvent, hymatomelanic acids were converted into the sodium form by dissolving in 0.02 M sodium hydroxide solution and precipitated by adding sulfuric acid to pH = 1.0. Then they were dried at a temperature of 35-40°C using forced ventilation.

The residue on the filter after alcohol extraction is humic acids, which constitute the main part of humic substances. It was dissolved in a minimum amount of 0.02 M sodium hydroxide solution, and then precipitated with sulfuric acid. In order to obtain a low-ash product, reprecipitation was carried out twice, after which the alkaline solution was passed through a cation exchange resin and dried.

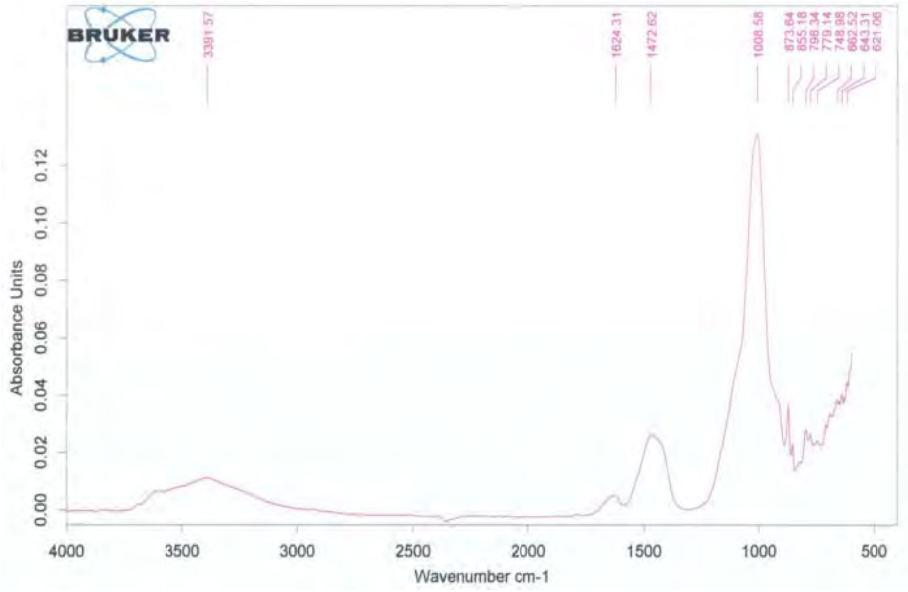
In order to obtain solutions of humic substances of peloids, accurately weighed portions of individual fractions of humic substances were poured with a certain amount of 0.05 M NaOH. A flask with the products was placed in a water bath, left for a day until the substance was completely dissolved. It was once filtered through a paper filter (white tape), the pH was adjusted to 7.4, and then diluted with purified water to 100 ml.

The yield of humic substances from therapeutic muds according to this method given in the scheme (figure 1) reaches 6-6.5%, which is identical compared to other similar papers [12].

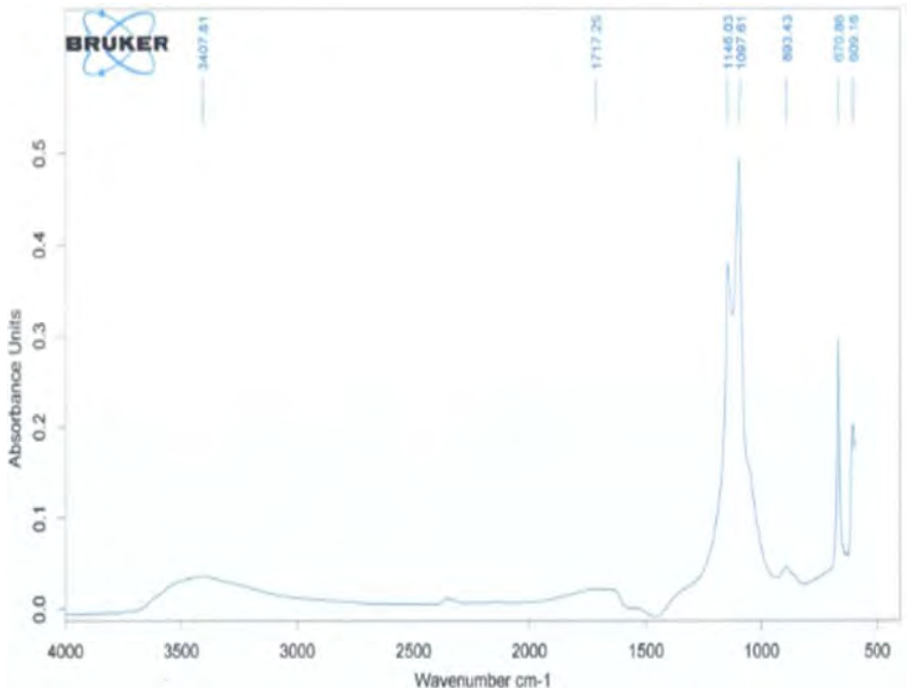
Further, using the IR spectroscopic method of analysis, we investigated the initial peloid and humic substances isolated from it using the method described above (figure 2). The analysis was carried out on the equipment named Tensor II by Bruker (USA), the spectra were recorded in the range of 600-3600 cm-^{1} using a diffraction grating.

Infrared spectroscopy has several advantages over spectroscopy in the visible and ultraviolet regions, since it allows tracing the changes in all the main types of bonds in the molecules of the substances under study. Taking into account the number and position of peaks in the IR absorption spectra, it is possible to estimate the nature of the functional groups of substances (qualitative analysis), and the intensity of the absorption bands — their relative quantitative ratio [13].

As can be seen from figure 2, 12 absorption peaks in the region of 3391-621 cm^{-1} were detected in the initial peloid spectrum, and only 7 peaks in the region of 3407-609 cm^{-1} were detected in the humic acid spectrum. According to the IR spectra of the initial peloid and humic acid isolated from it, common absorption bands in the region of 3400 cm^{-1} are revealed, which is caused by the



a)



b)

Figure 2 – IR spectra of a) initial peloid and b) humic substance of peloid

presence of primary amyls, which is manifested due to C=O vibrations of carbonyl of the amide group O=C=N, which indicates preservation of humic acids of individual protein fragments in the molecules. In the spectra of the peloid, the absorption bands in the region of 1625 cm^{-1} indicates the presence of a C=C bond conjugated with phenyl, the absorption band of 1475 cm^{-1} corresponds to stretch vibrations of the aromatic ring (pulsating vibrations of the carbon skeleton), the absorption band of 1008.58 cm^{-1} corresponds to aromatic compounds, planar deformation vibrations of C-H in the region of 1070-1000 (9.35-10.00) cm^{-1}, 5 peaks in the region of 873.64-748.98 cm^{-1} correspond to the nitro compounds R-NO_2 in the region of 920-830 (10.88-12.05) and to the nitrates of RO-NO_2 (variable intensity bands) and in the region of ~660 (~15.15) correspond to the nitrosamines R_2N-N = O, ~620 (~16.13) $\delta_{O=C-N}$, amides IV. The remaining 5 peaks related to both peloids and humic substances in the region of 693.43-609.15 cm-1 confirm the presence of alkynes ≡C–H. In the spectrum of humic acid, an absorption band appeared in the 1717.25 cm^{-1} region, which corresponds to the stretch vibrations of the carbonyl group, α, β-unsaturated C=C-COOH.

Analysis of the molecular structure of humic substances of peloids using IR spectroscopy showed that their macromolecule consists of frame olefin and aromatic fragments with a large proportion of unoxidized aliphatic groups, as well as the content of an aromatic structure with a significant content of carboxyl groups.

Conclusion. Thus, the proposed method for producing humic products from low-mineralized sulfide silt muds (peloids) makes it possible to obtain purified, therapeutically highly effective, ecologically-economically advantageous products for physical therapy in the conditions of resorts.

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Резюме

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ЛАЙ СУЛЬФИДТІ БАТПАҚТАН (ПЕЛОИД) ГУМИНДІК ЗАТТАРДЫ БӨЛІП АЛУ ӘДІСІ

Мақалада «Сақ» кен орнынан алынған лай сульфидті батпақтан гуминді заттарды бөліп алу әдісі сипатталған. Бұл әдіс бойынша емдік батпақтан бөлініп алынған гуминді заттардың шығымы 6-6,5% дейін жететіндігін көрсетті. Сонымен қатар бастапқы пелоид пен одан бөлініп алынған гуминдік заттардың ИҚ-спектроскопиялық талдауы зерттелді. ИҚ сіңіру спектрлеріндегі шыңдардың саны мен орналасуы қарай табиғи функционалдық топтар анықталды. Лай сульфидті батпақтан алынған (пелоид) гуминдік препараттарды бөліп алу әдісі арқылы шипажайлар жағдайында физиотерапия үшін тазартылған, терапевтикалық тиімділігі жоғары, экологиялық-экономикалық тиімді препараттар алуға мүмкіндік береді.

Түйін сөздер: лай сульфидті батпақ, пелоид, гуминдік заттар, фульво қышқылы, гиматомелан қышқылы, бөліп алу әдісі, «Сақ» кен орны.

Резюме

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СПОСОБ ПОЛУЧЕНИЯ ГУМИНОВЫХ ВЕЩЕСТВ ИЗ НИЗКОМИНЕРАЛИЗОВАННЫХ ИЛОВЫХ СУЛЬФИДНЫХ ГРЯЗЕЙ (ПЕЛОИДОВ)

Описан способ получения гуминовых веществ из Сакской низкоминерализованной иловой сульфидной грязи. Показано, что выход гуминовых веществ из лечебных грязей по данной методике достигает 6-6,5 %. А также ИК-спектроскопическим анализом исследованы исходный пелойд и гуминовые вещества, выделенные из него. По числу и положению пиков в ИК-спектрах поглощения определены природа функциональных групп веществ. Предлагаемый способ получения препаратов гуминового ряда из низкоминерализованных иловых сульфидных грязей (пелоидов) позволяет получить в условиях курортов очищенные, терапевтически высокоэффективные эколого-экономически выгодные препараты для физиотерапии.

Ключевые слова: иловые сульфидные грязи, пелойд, гуминовые вещества, фульвокислоты, гиматомелановые кислоты, методика, Сакское месторождение.