The American Journal of Applied sciences
(ISSN – 2689-0992)
Published: July 16, 2021 | **Pages:** 1-8
Doi: https://doi.org/10.37547/tajas/Volume03Issue07-01

IMPACT FACTOR
2021: 5. 634

OCLC - 1121105553

Journal Website: https://theamericanjournals.com/index.php/tajas

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Obtaining Humic Preparations From The Waste Of A Hydraulic Dump Of Coal Deposits As A Promising Waste-Free Technology

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ABSTRACT

Humic substances are the main organic component of soil and water, as well as solid fossil fuels. These important components are formed during the de-composition of plant and animal residues under the influence of abiotic envi-ronmental factors and as a result of the activity of microorganisms. In the future, humic substances are of great interest for medicine, veterinary medicine and plant protection as bioregulators, biostimulants and adaptogens, which deter-mine the normal functioning of various body systems. As a result of enrichment of coal from the Angren deposit, a large amount of waste accumulates, which negatively affects the ecological situation in the region and occupies large areas, in connection with which the question of their processing arises, in particular, to obtain humic preparations and bacterial fertilizers of prolonged action. The iso-lation of humic acids from the dumps was carried out with weak solutions of po-tassium and sodium hydroxides, and then precipitated from the obtained alka-line extracts by acidification with mineral acids to pH 2.0. In the residual cakes, the synthesis of humic acids was carried out by inoculation of an association of microorganisms BK 5 grown on rice flour. In the course of the research it has been found, that optimal separation of humic acid alkali consumption solvents NaOH or KOH is 8g per 100g of the crude product in a ratio of T:F = 1:5 at a temperature of 80° C for 30 minutes.

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KEYWORDS

Humic substances, coal mining waste, waste-free technology, humic acid, alkali, potassium and sodium humates, association of microorganisms BK 5, bacterial - humic fertilizers of prolonged action.

INTRODUCTION

Humic substances, as their name implies (from the Latin "humus" - soil), represent the main organic component of soil and water, as well as solid fossil fuels. These important components are formed during the decomposition of plant and animal residues under the influence of abiotic environmental factors and as a result of the activity of microorganisms, and their annual growth on the planet ranges from 0.6 to 2.5·109 tons per year [4]. In more. And. Vernad-sky spoke about the importance of humus as a product of the coevolution of living and nonliving planetary matter [1]. Stadnikov D.A., Who made a great contribution in the field of organic chemistry and Coal, characterized them as follows: "Humic substances are amorphous formation to obscure the structure of the light - to dark - brown color, are formed in nature by the decomposition of plant material, insoluble in benzene and showing a pronounced affinity for water, in which they dissolve or at least swell" [2,3].

According to the classification, based on the solubility of the humic sub-stances in acids and alkalis, they are divided into three components: humin - nonremovable residue, insoluble in any alkalis, neither in acids; humic acid - fraction, soluble in alkali and insoluble in acid (pH <2); fulvic acids - the frac-tion, soluble in alkalis, and acids. Humic and fulvic acids are, taken together, referred to as "humic acids", whose structure is shown in Figure 1. Humic ac-ids are high molecular weight compounds, having in their composition aro-matic nucleus, cyclic group, containing nitrogen, and peripheral chain and whose weight can reach 500,000 and characterized by high carbon content (52-62%), and fulvic acids belong to the type of hydroxycarboxylic acids and have a lower carbon content (44-49%) [5,6].

Humic acids are natural compounds that are of great scientific and prac-tical importance - they are primarily used as organic fertilizers and biostimu-lants, to increase soil fertility and increase crop yields. They also found appli-cation as sorbents, binders, metal corrosion inhibitors, in the production of highly concentrated coal-water slurries (VVWS) and as stabilizers for drilling fluids in the oil and gas industry. In the future, humic substances are of great interest for medicine, veterinary medicine and plant protection as bioregula-tors, biostimulants and adaptogens , which determine the normal functioning of various body systems [9, 10].

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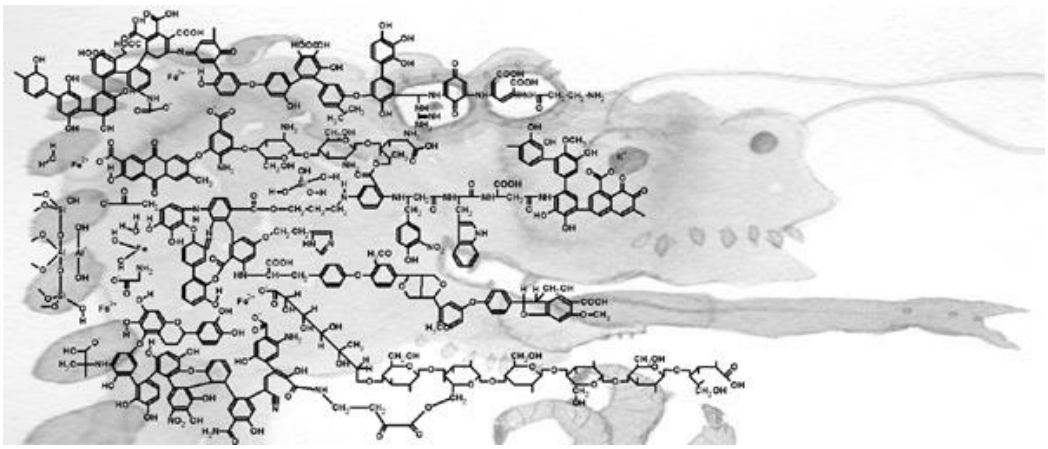

Fig.1. A hypothetical structural fragment of soil humic acids (Kleinhempel, 1970). Image: "Chemistry and Life"

Great opportunities for a wide variety of industries can open up with the use of chemically obtained humic preparations, including those from second-ary raw materials and waste.

Given the fact, that the enrichment of coal mine Angren has accumulated a huge amount of coal waste, pollutants during the weathering environment, highly relevant search methods for their efficient and economical processing. Meanwhile, these coal waste is a valuable secondary raw material for various products, primarily for the production of organic fertilizers. This aspect leads to the need to develop a waste-free technology in order to obtain humic acids and bacterial humic fertilizers of prolonged action.

MATERIALS AND METHODS

The tests were carried out on an average sample of the waste from the hydraulic dump of the coal mining of the Angren deposit. The beneficiation process (in order to reduce ash content) consists in washing coal with water, as a result of which coal dust and mineral particles are removed. The resulting slurry flows through pipelines to the tailing dump, where, with the loss of wa-ter, "tailings" of coal preparation are formed. This mixture of coal and mineral particles is called clay - carbonaceous sludge In fact, the mineral component of this mixture, according to the granulometric analysis, varies from sandy - silty clays to clay - sandy silts. Macroscopic sludge - is a loose gray - black weight, a bulk density of 1.4 g/cm3, characterized by the heterogeneity in the composi-tion and cross-sectional area dumps - with varying ash content and corre-spondingly with varying organic matter content. In the mineral component, the main rock-forming minerals are quartz and clay minerals, the minor ones are rock fragments. Clay minerals are represented by hydromica - kaolinite associ-ation with a predominance of kaolinite over hydromica.

The isolation of humic acids from the waste of the coal mine was carried out with weak solutions of alkalis and then precipitated from the alkaline ex-tracts by acidification with mineral acids (approximately to pH 2.0). The syn-thesis of humic acids in residual cakes was carried out by inoculating an asso-ciation of

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microorganisms BK 5 grown on rice flour. The complete chemical analysis of samples and the average results for selected metals content (g/t) by the method of mass - spectrometry analysis (ICP-MS) was carried out in the SE "Central Laboratory". Determination of the content of humic acids was de-termined at the State Institution "Institute of Mineral Resources".

RESEARCH RESULTS AND THEIR DISCUSSION

For a complete chemical analysis of the average sample of the waste dump. The results obtained are characterized by a relatively low content of SiO2 -34.74%, FeO -2.62, a sharp predominance of potassium (K2O -1.18%) over sodium Na2O -0.40 %. Other elements, such as magnesium, calcium, iron, sulfur, manganese, though in small amounts provide a favorable back ground, needed for plant growth.

Table 1

Results of a complete chemical analysis of an average sample of hydraulic dump waste

№	Component name	Content, %	№	Component name	Content, %
1	SiO_2	34,74	10	K_2O	1,18
2	Fe_2O_3	1,90	11	P_2O_5	0,18
3	FeO	0,72	12	$S_{общ.}$	0,83
4	TiO_2	0,46	13	п.п.п.	40,46
5	MnO	0,12	14	сумма	98,81
6	Al_2O_3	13,54	15	CO_2	0,02
7	CaO	3,30	16	SO_3	1,04
8	MgO	1,7	17	H_2O	4,64
9	Na_2O	0,40	18	$S_{sulfide.}$	0,41

Table 2 presents the results for the elements - impurities in the secondary hydraulic dump waste sample by mass - spectrometry analysis (ICP - MS). In the average sample of the waste dump, the content of biologically valuable microelements was established - zinc - 210 g/t , copper - 32.0 g/t , boron - 28.0 g/t , manganese - 140 g/t. Of the toxic elements, arsenic -32 g/t is present in the average sample of the waste dump. The content of arsenic exceeds its clarke in sedimentary rocks by 3 times. However, such arsenic contents are environmentally friendly.

Table 2.

The results of individual metal content (g/t) in the central hydraulic dump waste sample by mass - spectrometry analysis (ICP - MS)

The elements	Initial sample	The elements	Initial sample	The elements	Initial sample	The elements	Initial sample
Li	65 , 0	Ni	7.50	Sn	2 , 10	Er	1.40
Be	1.50	Cu	32.0	Sb	2.80	Tm	0.210

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B *	28.0	Zn	210	Te	< 0.30	Yb	1.40
Na *	1200	Ga	12.0	Cs	35.0	Lu	0.190
Mg *	2800	As	32.0	Ba	560	Hf	2.20
Al *	21000	Se	1.60	La	29.0	Ta	1.00
P	480	Rb	92.0	Ce	44.0	W *	15.0
K *	10000	Sr	130	Pr	5.80	Re	< 0.01
Ca *	8400	Y	12.0	Nd	20.0	Pt *	< 0.05
Sc	6.2	Zr *	64.0	Sm	3.80	Au *	0.140
Ti *	2200	Nb	10.0	Eu	0.790	Tl	0.870
V	60.0	Mo	9.10	Gd	3.30	Pb	54.0
Cr	37.0	Ag	0.410	Tb	0.470	Bi	0.480
Mn	140	Cd	0.230	Dy	2.80	Th	12.0
Fe *	7400	In	0.061	Ho	0.460	U	4.80
Co	4.10						

Considering, that humic acid soluble alkaline solvents all studies based on the use of two solvents alkali: NaOH (dissolution of humic acids in the form of sodium humate) and KOH (dissolution of humic acids as the potassium humate).

In order to determine the optimal conditions for the release of humic acids, two schemes were worked out.

Scheme I. Coal mining wastes were pretreated with alkaline solutions of NaOH with different consumption of alkali per unit weight of the processed product. After separation of the solid solution, containing dissolved humic acid as sodium humate, a solid (cake I) after 3- fold washing with water have been reported in bacterial processing step for obtaining bacterial fertilizer.

The solution with sodium humate was combined with wash water, after which it was acidified with sulfuric acid to pH 2.0, while humic acids precipitated, which was washed with water. After separation of humic acids, the solution was passed through a paper filter, the precipitate was dried, weighed, and the percentage of HA was determined. The experiments were carried out at different temperature conditions, contact time with alkali, and S:L ratio. The optimal regime for extraction of humic acids become: T:F = 1:5, t 80°C and a contact time of 30 minutes. The data on the optimal alkali addition are shown in Fig.2.

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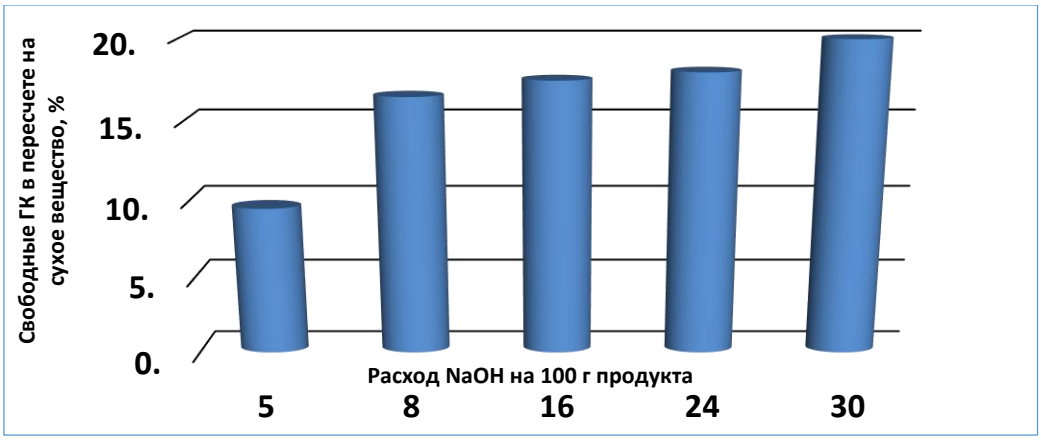

Fig.2. Determination of the optimal consumption of sodium hydroxide for the extraction of humic acids.

According to the results of the experiments, the most technologically acceptable result was obtained with the addition of 8g of NaOH per 100 of the starting product.

Scheme II. Coal wastes were pretreated with K OH alkaline solutions with different alkali consumption per unit weight of the processed product. After separation of the solid solution, containing dissolved humic acid in the form of potassium humate, a solid (cake II) after 3- fold washing with water have been reported in bacterial processing step for obtaining bacterial fertilizer.

The solution with potassium humate was combined with wash water, after which it was acidified with sulfuric acid to pH 2.0, while humic acids precipitated, which was washed with water. After separation of humic acids, the solution was passed through a paper filter, the precipitate was dried, weighed, and the percentage of HA was determined. The experiments were carried out at different temperature conditions, contact time with alkali, and S:L ratio. The optimal regime for extraction of humic acids become: T:F = 1:5, t 80°C and a contact time of 30 minutes. The data on the optimal alkali addition are shown in Fig.3.

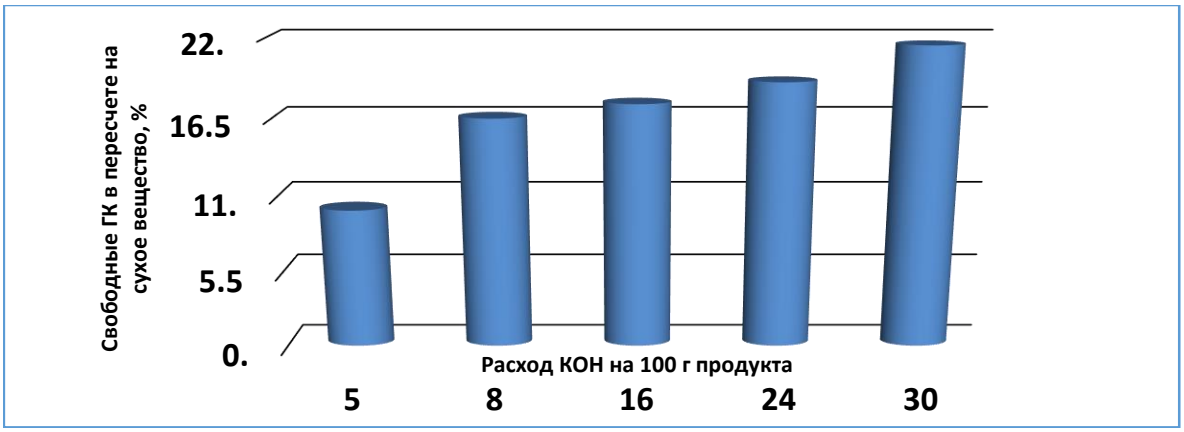

Fig.3. Determination of the optimal consumption of sodium hydroxide for the extraction of humic acids.

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According to the results of the experiments, the most technologically acceptable result was obtained with the addition of 8g KOH per 100 starting product.

Fig.4. Received liquid and powdery humic preparations.

CONCLUSION

In the course of our investigations have shown, that the optimal conditions for the isolation of humic acids in the art are handling 8g per 100g of alkali solvents starting material NaOH or KOH, the ratio of T:F = 1:5, an optimum T - 80 C°, contact time -30 min. An increase in alkaline solvents increases the transfer of humic acids, but leads to difficulties in the decantation process, thereby increasing the stage of washing and increasing the time of the technological process.

By the results obtained it can be concluded, that at processing of one ton of waste can be obtained the hydraulic dump 165 kg humic acid and 835 kg of residual cake, which after 3 fold washing water supplied to the bacterial treatment stage to obtain a bacterial fertilizer.

One of the possible ways to create an integrated technology for the processing of coal mining wastes is the creation of a waste-free scheme for processing coal mining wastes with the parallel release of humic acids and the production of humic fertilizers of prolonged action from the waste after HA extraction.

In connection with the increasingly aggravated environmental situation, the development and application of such an integrated technology for the processing of hydraulic dumps will not only make it possible to obtain valuable high quality products at a low cost of the process, but also to eliminate the source of anthropogenic pollution.

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