

# Humic Acids of Caustobioliths as the Basis of Novel Materials for Environmental Protection and Green Construction

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## Abstract

Results are presented concerning the studies on the properties of preparations obtained via colloidal chemical separation of humic acid salts. A considerable difference is demonstrated in the properties of humic preparations isolated from acidic and alkaline media, and, first of all, in changing the elemental composition of humic preparations, as well as in the composition and proportion between functional groups in the molecular structure of the mentioned compounds. Results of determining the sorption activity of humic preparations obtained for the sorption of ions from mono-ionic and binary solutions are presented. The regularities revealed have been assumed as the basis for creating some novel sorption and soil-reclamation materials of nature conservation purposes.

**Key words:** humic acids, humic substances, functional groups, sorption, heavy metals, soil-reclamation preparations

## INTRODUCTION

Humic substances (HS) play an exclusive role in life of the nature and of a man. For example, due to the use of HS in the engineering ecology, potentialities of this class of natural polymers and preparations based on them have become clear and vindicated as a tool allowing one to solve a wide range of the problems concerning the environmental control. Humic substances represent a wide class of compounds those perform required mediatory functions between the living and mineral worlds. So, dark colouring of HS is directly connected with the regulation of thermal conditions in soils as well as the climate of the Earth as a whole. The polyfunctionality of HS provides them to exhibit a dominating role in the accumulation and migration of metal ions in soils and terraneous

landscapes. Specific hydrophilicity and molecular structure predetermine the HS uniqueness as structure-forming components of soils, as a regulator of soil air and water regime, as a means for reclaiming the territories disturbed by economical activities of a man, *etc.* [1, 2].

Under contemporary conditions the world economy becomes a united economy with all the consequences, wherefrom any country (including Russia, too) is required to actively participate in the International cooperation, as well as to concentrate the efforts for the realization of effective projects having a prospect of commercialization on the basis of advanced achievements of science and technology. In this connection the export orientation represents just the starting moment that provides an equal right International economic and technological cooperation. Technologies concerning the recon-

struction of sustainable agricultural ecosystems in the territories disturbed due to human economic activities (including deserted territories), with the use of meliorative preparations (soil improving agents) on the basis of peat, sapropels, lignin, brown coal, and other kinds of regional organic raw material could be considered to be export-oriented projects to a complete extent. In this case the article of export is presented not only by materials, but also an entire complex of high technologies providing a meliorative ("green") arrangement of lifeless territories. At the same time among the naturally occurring minerals of biogenic origin, such raw as peat, sapropels, lignin, and brown coals form the basis for raw material resources of the Republic of Belarus, which, naturally, obliges scientists to find novel methods for their processing.

Humic acids (HA) are considered to be a main component of HS. Being natural polymers, these substances represent a wide class of homologues consisting of compounds those differ from each other in structure, composition, amount and topography of molecular fragments. Depending on the genesis of raw material and its metamorphic level, both high-molecular and low-molecular compounds with different content of aliphatic and aromatic fragments, functional groups could prevail in the composition of HA. Therefore HA isolated from various kinds of raw material, differ from each other in composition and properties. Under dehydration and drying the structure of HA fragments is also undergone to a considerable transformation with changing both the composition of active centres of HA associates, and the physicochemical properties of a preparation as a whole.

A high exchange capacity of HA offers outstanding possibilities for manufacturing on their basis ion-exchange sorption materials based on these substances purposed for waste and technological waters purification from heavy metal ions [3, 4].

A specific conglomerate of the properties inherent in a combined lipophilic-and-hydrophilic structure of HA provides the mentioned class of naturally occurring polymers to be promising for employing them as selective sorbents for non-polar hydrocarbons in natural media [5].

A high hydrophility of HS from natural caustobioliths offers almost unlimited possibili-

ties in order to develop ion-exchange soil-reclamation materials on their basis for reclaiming the territories disturbed by human economic activities, first of all the territories contaminated with heavy metals, radionuclides [3–5]. Thus, the processes of HA complex formation with the ions of polyvalent metals determine to all intents and purposes both the technology for obtaining humic preparations (HP) with a selective action, and the field of their practical application.

## EXPERIMENTAL

The tendency towards association and, on the contrary, to dissolution depends on the functional composition and molecular structure of HA. In their structure one can observe oxygen-containing functional groups to prevail, first of all carboxylic groups. The higher the content of functional groups in structure of a compound, the higher is its affinity with respect to a polar solvent, and consequently, its solubility. Owing to the prevalence of non-polar fragments, hydrophobic properties of the compound tend to increase, thus its solubility should increase. As a result, the compounds of hydrophilic nature under dissolution in water tend to form true solutions, whereas hydrophobic substances use to form colloidal solutions. Thus, there is a molecular-disperse equilibrium taking place in the solution: true solution  $\leftrightarrow$  sol  $\leftrightarrow$  gel  $\leftrightarrow$  colloidal associate structure. Just for this reason the fractions HA exhibit different molecular associate structure. In this connection we performed the fractionation of the HA from peat according to their water-solubility depending on the pH value of the medium, according to their ability to be dissolved in water within a certain range of the solution pH [6].

Using the method of differential potentiometric titration we have determined the content of the functional groups capable to participate in exchange processes. The ionic strength of the solution was maintained at a required level using 0.2 M NaCl solution. The dissociation degree for the compounds under investigation was determined according to the curves of potentiometric titration obtained for HA solution and reference solution. Basing on the data of potentiometric titration we calcu-

lated the values of dissociation constants for functional groups of HA fractions according to the Henderson–Hasselbach equation [1].

The nature of active centers was studied using a set of 24 acid-base indicators operating within the  $pK_a$  range from 4.4 to 14.2. Preliminary we dried HA to obtain a constant mass at the temperature of 60 °C, grinded it by means of an agate mortar and bolted them using a set of sieves. For the analysis we used a fraction with the particle size  $\leq 0.25$  mm [7].

The phase state of HA was assessed using an XRD method. XRD profiles of the objects under investigation were registered employing an HZG-4a diffractometer ( $CuK_\alpha$  radiation, Ni filter) at the scanning rate of a scintillation counter of quanta equal to 0.02 grad/min, for the angles ranging within 5–50  $2\theta$  grad. Samples for the registration were prepared by means of a pressing method.

## RESULTS AND DISCUSSION

The increase in the dissociation degree of HA fractions with the increase in the solution pH could be explained by the transition of HA solutions from the association colloid state to the true solution state, which results in increasing the ability of HA functional groups for exchange process as well as in increasing the reactivity of HA fragments. From the data obtained (Fig. 1, Table 1) it follows that the content of dissociated functional groups in the fractions correlates with the content of oxygen in HA structure. The exchange capacity exhibits a maximal value for fraction No. 6 and a minimal value for fraction No. 1, containing minimal

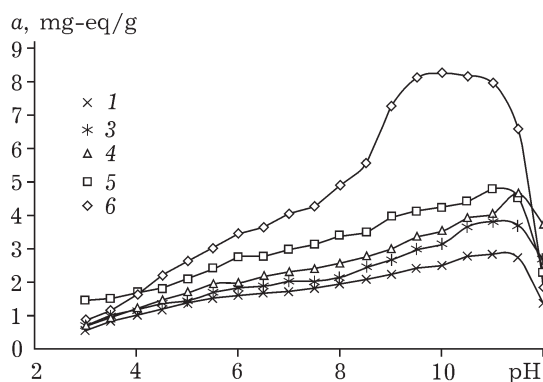


Fig. 1. Variation in the exchange capacity of HA fractions depending on the solution pH: 1, 3–6 – denote fractions Nos. 1, 3–6, respectively.

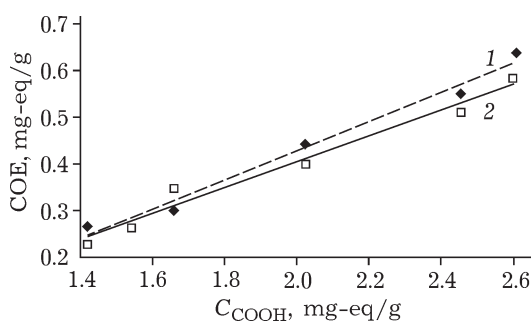


Fig. 2. Dependence between the content of carboxyl groups in HA fractions and their static exchange capacity (SEC) for ions  $Cu^{2+}$  (1) and  $Ni^{2+}$  (2) at  $pH \leq 4$ : 1 –  $SEC(Cu^{2+}) = 0.3102C_{Cu^{2+}} - 0.194$ ,  $R^2 = 0.9877$ ; 2 –  $SEC(Ni^{2+}) = 0.2767C_{Ni^{2+}} - 0.1487$ ,  $R^2 = 0.9759$ .

oxygen amount (within oxygen-containing functional groups).

The analysis of the data obtained demonstrates that the static exchange capacity (SEC) for HA fractions with respect to  $Cu^{2+}$  and  $Ni^{2+}$  ions at  $pH \leq 4$  is in direct dependence on the content of carboxyl groups in the structure of HA (Fig. 2). One can see that under these con-

TABLE 1

Elemental composition of HA fractions

Fraction No.	pH	Elemental composition of the organic mass, %					C/H
		C	H	N	S	O	
1	11.0–12.7	65.4	8.0	2.6	0.9	23.1	0.68
2	10.0–11.0	63.2	7.6	2.7	0.9	25.6	0.70
3	8.0–10.0	62.1	7.3	2.5	0.9	27.2	0.71
4	6.0–8.0	61.0	6.3	1.4	0.9	30.4	0.81
5	3.8–6.0	60.7	6.2	1.3	1.0	30.8	0.82
6	2.0–3.8	57.9	5.7	1.2	1.1	34.1	0.84

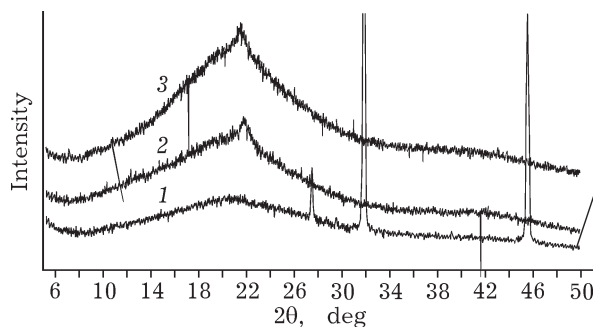


Fig. 3. XRD profiles of HA fraction No. 5: 1 - H-HA; 2 - HA, purified *via* dialysis in distilled water; 3 - the same in acidic medium (0.1 M HCl).

ditions the values of SEC for  $\text{Cu}^{2+}$  and  $\text{Ni}^{2+}$  ions are almost coinciding [8].

As far as the phase state is concerned, all the samples HA fractions HA are in the amorphous state according to the data of XRD analysis. The three intense signals (Fig. 3, curve 1) within the range of reflection angles  $2\theta$  (27.3–27.5, 31.6–31.8, 45.3–45.6) might be attributed to a residual impurity of NaCl in the sample, caused by the specificity of HA isolation. However, in the case of the acidic form of HA purified by means of dialysis one can observe a tendency towards ordering the structure, which, to all appearance, is connected with the absence of HA ionization as well as a compact localization of proton. As a consequence, the

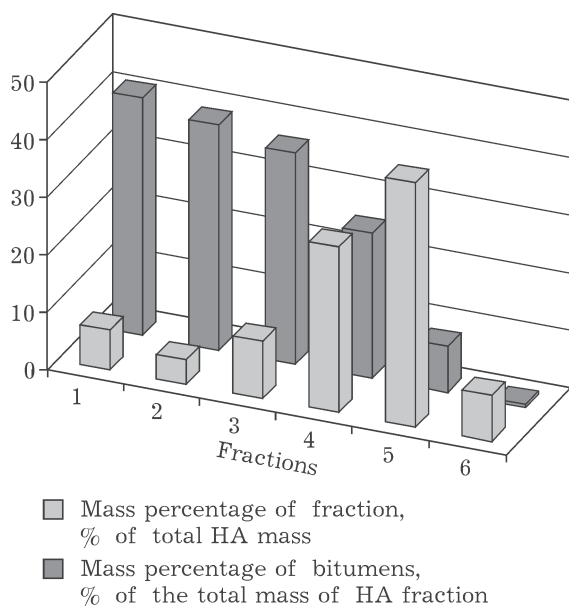


Fig. 4. Specific content of HA fractions and the mass percentage of bitumen content therein [10].

steric hindrances with respect to HA ordering in the H-form of HA are much less, however, no formation of HA crystallization structures is observed to occur. The XRD phase analysis has revealed in HA no polysaccharide HA precursor such as cellulose in any modified form, too [9].

The amount of substances soluble in chloroform is reduced with going from fraction No. 1 to fraction No. 6 (Fig. 4), which could be explained by an increase in hydrophilic properties, as well as by the content of ionogenic functional groups and polar fragments (see Table 1, C/H and O/C ratio values). On the contrary, with the increase of pH one can extract from humic raw material the HA those exhibit more expressed lipophilic properties. In this case the content of H in HA fractions correlates with the bituminosity (the correlation coefficient being equal to 0.94).

The distribution spectra for HA acid-base centres are presented in Fig. 5. Since the structure of HA contains functional groups in various forms, the peaks obtained allow us to determine the character (or the condition) of functional groups. The data presented in Fig. 5 indicate the prevalence of functional groups for those the value of  $\text{pK}_a$  is equal to 2–3.5 and 12.8–14, corresponding to the carboxyl and hydroxyl groups, respectively. Changing the conditions of HA isolation results in changing the condition of functional groups. In going from fraction No. 3 to fraction No. 5 the value of acidity function  $H_0$  increases from 8.8 to 12.9.

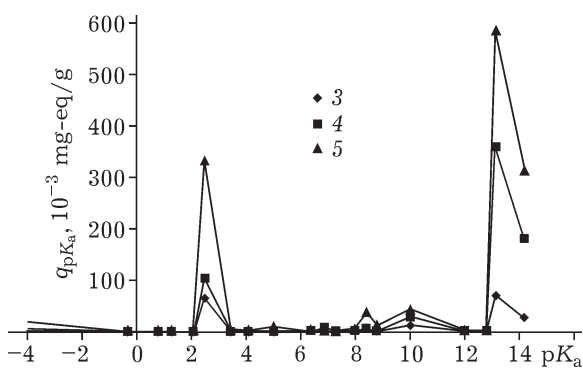


Fig. 5. Distribution spectra for active centres on HA powder aggregates depending on the ionization constant of ionization  $\text{pK}_a$  for functional groups: 3–5 denote fractions Nos. 3–5, respectively.

TABLE 2  
Characteristics of functional groups of HA fractions

Fraction No.	Functional group	<i>m</i>	p <i>K<sub>a</sub></i>
1	-OH	0.4094	8.59
	-COOH	2.2523	5.91
3	-OH	0.4351	8.59
	-COOH	2.1044	5.72
4	-OH	0.5891	9.26
	-COOH	1.4733	5.08
5	-OH	0.9301	9.70
	-COOH	1.3577	4.96
6	-OH	0.9234	8.32
	-COOH	0.6424	4.22

The reduction of the titration parameter *m* (Table 2), describing the electrostatic interaction between functional groups in HA, in going from fraction No. 1 to fraction No. 6, could be connected with the reduction of the size of HA aggregates in the case of the carboxyl groups. The mentioned reduction, most likely, could occur due to a decrease in the length of aliphatic HA fragments. This hypothesis is confirmed by the fact, that the p*K<sub>a</sub>* value for the carboxyl groups in HA structure decreases.

In order to study the regularities in the interaction of HA with the ions of polyvalent metals we employed water-soluble salt-like forms of HA. The interaction of such ions as Fe<sup>3+</sup>, Cu<sup>2+</sup>, Zn<sup>2+</sup>, Ca<sup>2+</sup>, Sr<sup>2+</sup> with salt-like forms of HA has been experimentally investigated. It has been established, that the precipitation of the products resulted from the reac-

tion between salt-like forms of HA and polyvalent metal ions depends both on the nature of a cation, and on the concentration of the salt-like forms of HA, whereas the coagulation begins when a certain critical cation concentration is reached in the solution. The critical concentration value for the solutions of the salt-like forms of HA (in going from Fe<sup>3+</sup> to Sr<sup>2+</sup>) is an order of magnitude increased. In this case the purification level of the solution decreases from 92 % (for Fe<sup>3+</sup>) down to 20 % (for Sr<sup>2+</sup> and Ca<sup>2+</sup>), whereas the complex formation activity of HA correlates in a simbasic manner with the ion potential of an adsorbed metal, *i.e.* the higher ion potential of the metal, the higher is the purification level of the solution (Table 3).

The HP were observed to bind first of all Fe<sup>3+</sup> and only in small amounts Cu<sup>2+</sup> from the binary solution of trivalent iron and bivalent copper salts, which could be caused both by the value of the ion potential of copper cation, and by its condition due to its staying within the solution. In the binary solutions Cu-Zn, Cu-Sr and Cu-Ca the HP mainly react with copper ions, whereas the concentration of Zn, Sr, and Ca in the solution remains almost constant.

The basic point for water purification from metal ions consists not only in the formation of an HA-metal complex, but also in removing the complexes from the solution. At low concentrations of polyvalent metal ions the organic-and-mineral water-insoluble complexes formed are

TABLE 3  
Critical concentration of ions corresponding to the coagulation of salt-like HA forms

Cations	Critical	Purification	Ion potential
	concentration, mg-eq/L	level, %	
Fe <sup>3+</sup>	2.1	92	4.5
Cu <sup>2+</sup>	3.8	88	2.5
Zn <sup>2+</sup>	7.1	24	2.4
Ca <sup>2+</sup>	25.0	20	1.9
Sr <sup>2+</sup>	25.0	20	1.6

TABLE 4  
Purification level of solutions depending on the ratio between the concentrations of a polyvalent metal ion and of humic complex-forming agent

Fe <sup>3+</sup>		Cu <sup>2+</sup>	
<i>C<sub>Me</sub></i> / <i>C<sub>sorb</sub></i>	Purification level, %	<i>C<sub>Me</sub></i> / <i>C<sub>sorb</sub></i>	Purification level, %
0.018*	98	0.050*	96
0.020*	92	0.058*	96
0.023	92	0.071	91
0.032	82	0.096	83
0.047	64	0.141	70
0.050	63	0.150	64

\*Limiting concentrations those result in the excess of a humic complex-forming agent in the solution of a solution there is a surplus humic complex-forming agent.

stabilized either by metal ions or by polar groups of HA, wherefrom they do not form compact structures. And, on the contrary, when the concentration of polyvalent metal ions is equivalent to the content of corresponding functional groups in HP (capable of forming the complexes), one can observe the formation of compact structures with a greater level of structural order. Both of these states are inherent also in a humic complex-forming agent (Table 4).

One can see that for iron ions of the optimum ratio between the concentration of metal and the concentration of humates in the initial solution is equal to 0.023, whereas for copper ions this value amounts to 0.071. At a lower  $C_{Me}/C_{sorb}$  ratio, there is an excess of a humic sorbent remaining in the solution.

In order to estimate the influence of ionic strength of the solution upon the selectivity and the efficiency of metal ion interaction with salt-like forms of HA we studied the sorption of copper ions by HP in the presence of NaCl (the ionic strength ( $\mu$ ) of the solution was varied from 0.005 to 0.4),  $CaCl_2$  ( $\mu = 0.006-0.03$ ),  $AlCl_3$  ( $\mu = 0.003-0.06$ ). It has been established that increasing the ionic strength of the solution results in reducing the sorption of ions by salt-like HA forms. In this case, as the ionic strength increased from 0 to 0.03 the sorption of copper is by 22 % reduced in the presence of NaCl, 52 % reduced in the presence of  $CaCl_2$  and 58 % reduced in the presence of  $AlCl_3$ . With increasing the ion potential of metal in complex solutions, the sorption of copper ions (at the same ionic strength of the solution) is the lower the higher is the ion potential of the ions of a concurrent metal.

## CONCLUSIONS

Thus, the results of experimental investigations concerning physicochemical and colloid-chemical properties of HA indicate the uniqueness of the properties of the mentioned class of naturally occurring compounds as well as the possibility for employing them in solving the problems of environmental protection.

1. As a whole, the higher is the molecular mass of HA fraction or of its salt-like form, the higher is also the HA efficiency as a complex-forming agent, *i. e.* as a depressor for the

transport of polyvalent metal ions in aqueous media and soil systems. At the same time, the higher ion potential of a polyvalent cation, the more pronounced is its tendency towards complex formation with HA, with its salt-like forms and, first of all, with Na-HA, whose SEC value is maximal.

2. On the basis of the aforementioned studies performed within the framework of the State Program "Low-Tonnage Chemistry" for the period of 2004–2008, a manufacture was developed and organized in the Republic of Belarus involving the production of more than 10 novel materials for environmental control, namely: sorbents for heavy metal ions; humic reclaiming agents for soils contaminated with heavy metals (radionuclides); humic reclaiming agents for sandy soils and the territories disturbed by human economic activities; reclaiming agents for salted soils with for the purpose of their "green" arrangement; other materials for solving the problems of environmental protection based on HS from natural caustobioliths or their agglomerated compositions modified with salt-like forms of HA, *etc.*

Among the listed above materials the greatest economic effect is provided by meliorative kinds of products finding a steady market in the Persian Gulf States. In this connection, since 2004 the preliminary batches of meliorative products have been supplied to such countries of the Arabian region as United Arab Emirates, the Kingdom of Bahrain, Qatar, Jordan for the purpose of registering and certifying them in the mentioned countries. The manufacture of export-oriented production has been organized at the raw-material and production base of the Zhitkovichskoye Enterprise and the AridGrow Production Ltd. At the last exhibition in Dubai (November, 2008) the presented HP of meliorative purposes received a high appreciation from the Arabian experts who demonstrated their interest in increasing the volume of export of these preparations, as the materials for green construction.

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