

# Hybrid Biopolymer Nanocomposite Materials for Ecological and Biomedical Applications

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**Abstract**— This article developed and studied new hybrid biopolymer nanocomposites based on polylactide and humic substances. It has been established those humic substances, which were obtained from brown coals by four different extraction methods, are characterized by nanodispersion in the range of 52 – 380 nm. It was found that the presence of these functional groups determines the ability of humic substances to act as a hybrid modifier of polylactide: conformational changes in its secondary structure and dipole-dipole interaction in the form of a hydrogen bond. Due to the increase in the degree of crystallization and the emergence of intermolecular and ester bonds in the formation of a more rigid network structure in the polylactide-humic substances system, there is an increase in mechanical properties of hybrid biopolymer nanocomposite materials. Also, based the obtained hybrid biopolymer nanocomposite materials based on polylactide and nano disperse humic substances can be used to produce membrane-covering materials for wounds, implants, medical devices and products for dermatological treatment.

**Keywords**—nanocomposite, hybrid, biopolymer, humic, biomedical applications

## I. INTRODUCTION

In the last 10-15 years, hybrid polymer nanocomposite materials with biological activity have become widespread [1, 2]. They have important areas of application not only in modern nanomedical technologies and drugs but also in the processes of purification and bioremediation of hydrocarbon-contaminated various environmental objects, adsorption, separation and storage of gas, catalysis, sounding, electronic devices and more. Such polymeric hybrid nanocomposite materials have attracted attention due to their special structural and surface characteristics, which determine such a wide range of functional applications. The biological "tool" of hybrid polymeric nanocomposite materials is immobilized in a polymeric carrier of microorganisms or biologically active substances of organic and inorganic nature [3]. Functionalization of polymer surfaces of hybrid polymer nanocomposite materials is usually provided by chemical or covalent bonds, low energy interactions [4–5], non-covalent physical attraction, such as adsorption of contaminants [6,7], antibacterial biomaterials [8– 10] and drug delivery systems [12–13].

The nature of the polymer matrix and bioactive components and the conditions of their formation is especially important when creating hybrid polymer nanocomposite materials. These factors ultimately affect the formation of an effective nanocomposite structure of hybrid polymer nanocomposite materials and their performance characteristics. In this regard, the use of various inorganic and organic functional materials with nanoscale particle sizes in the creation of hybrid polymer nanocomposite materials is very perspective, as, first, the high dispersion of the particles allows to ensure their uniform distribution in the matrix, which can be achieved improved physical and mechanical properties, secondly, a high degree of homogenization of mixtures of components simplifies the technological process of their processing, thirdly, combining the optimal volume content of components of hybrid polymer nanocomposite materials, you can create compositions with the necessary magnetic, sorption, dielectric and other special properties. In this case, hybrid polymer nanocomposite materials may not only use one or more special functions but also provide modularity of materials through a combination of functional components. A perspective direction for the design of hybrid polymer nanocomposite materials based on a functional hybrid modification of polylactide with humic substances. Mixtures of polylactide with humic substances are interesting because of their potential application as biomedical frameworks for the production of adsorbents of pollutants and heavy metal ions, antibacterial biomaterials, drug delivery systems, sorbents of oil-containing natural, industrial and domestic waters, etc. It has been found [14] that heavy metal ions pollution can be reduced by ion exchange, complexation and surface adsorption with the participation of humic substances, while even persistent organic pollutants are first adsorbed and then decomposed by reduction-oxidation processes. About the functional action of humic substances, it should be emphasized that the binding of ions in them is special and expands the capabilities of conventional ion exchange resins [15].

Carboxylate groups of humic substances bind ordinary ions ( $\text{Na}^+$ ,  $\text{K}^+$  or  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Fe}^{2+}$ ) due to Coulomb interactions, while phenolic and phenolate groups are extremely effective for chelation of metal ions (all d-elements, especially  $\text{Fe}^{3+}$ ). In addition, hydrated ions in the

form of phosphate bind through H-bridges and surface adsorption ("hydrophobic" effect).

In our previous works [16, 17] we studied humic substances as structuring and antimicrobial agents in different types of biopolymers. In this work, the creation of hybrid polymer nanocomposite materials based on humic substances and biopolymer polylactide, which was previously studied by us [18-20].

## II. THE PURPOSE AND OBJECTIVES OF THE STUDY

The purpose of this work was to study hybrid biopolymer nanocomposite materials for environmental and medical applications

The objects of study were:

- plastic bland of PLA Terramac TP-4000;
- humic substances, were obtained by extraction of brown coal. Table 1 shows the conditions of the research, namely: the procedure and determination of the yield of toluene extract and free humic acids. Option "0". Determination of toluene extract. The essence of the method is as follows: a portion of brown coal is extracted with toluene in an extraction apparatus. The solvent is then distilled off, and the dissolved residue is dried to constant weight. The yield of toluene extract in per cent is calculated by the mass of the residue after drying, the result is given to the dry state of the fuel.

Option "1". Compared to option "0", the weight of the sample and the volume of solvent were increased. Instead of the extraction apparatus, the following heating scheme was used:

1. One-time heating to  $\sim 100^{\circ}\text{C}$ ;
2. Heating for 6 hours in an oven at  $40\text{-}50^{\circ}\text{C}$ ;
3. Maceration for 18 hours at  $20\text{-}22^{\circ}\text{C}$ ;
4. Single heating  $> 70^{\circ}\text{C}$ .

All brown coal remaining after the determination of the yield of toluene extract was used to determine the yield of free humic acids. Due to the increased mass of the brown coal sample, the concentration and volume of NaOH for both boiling and leaching was almost doubled.

Option "2". The yield of free humic acids was determined before the determination of toluene extract. All procedures were identical to option "1".

Option "3". The yield of free humic acids was determined before the determination of toluene extract. The method for determining the yield of humic acids was identical to options 1 and 2. Determination of toluene extract was performed using an extraction apparatus, the volume of toluene reached  $230\text{ cm}^3$ . Performed the determination of toluene extract from humic acids was similar to item 1, namely using an extraction apparatus, the volume of toluene reached  $230\text{ cm}^3$ . The yield of free humic acids was determined according to [21].

The extraction apparatus used to determine the toluene extract is shown in Fig. 1. The extraction apparatus is a nozzle that allows you to extract the maximum amount of the desired substance from solid or liquid raw materials using volatile solvents. The extraction apparatus consists of the following parts: a flat-bottomed conical flask with a capacity

TABLE I. CONDITIONS OF PERFORMANCE OF RESEARCH

Stage	Option			
	0	1	2 <sup>a</sup>	3 <sup>a</sup>
1. Determination of the yield of toluene extract				
1.1 Mass of portion of sample, g	17.216	26.736	14.823	10.234
1.2 Volume of toluene, cm <sup>3</sup>	150	230		
1.3 Conditions of extraction	4 hours in the extraction apparatus	1. Single heating $\sim 100^{\circ}\text{C}$ . 2. 6 hours in the oven at $40\text{-}50^{\circ}\text{C}$ . 3. Maceration during 18 hours at $20\text{-}22^{\circ}\text{C}$ . 4. Single heating $> 70^{\circ}\text{C}$		4 hours in the extraction apparatus
2. Determination of the yield of humic acids				
2.1 Mass of portion of sample, g	3.646	22.752	26.37	26.227
2.2 Volume of NaOH, cm <sup>3</sup> (%)	100(1)	200(2)		
2.3 Boiling in a water bath, hour	2			
2.4 Leaching The volume of NaOH (%), cm <sup>3</sup>	$2 \times 100(1)$	$2 \times 165(2)$		
2.5 Volume of HCl, cm <sup>3</sup> (%)	60(5)			
3. Determination of the yield of toluene extract from humic acids				
3.1 Mass of portion of sample, g	Not determined			13.030
3.2 Volume of toluene, cm <sup>3</sup>				230
3.3 Conditions of extraction				4 hours in the extraction apparatus

<sup>a</sup> stage 2 was performed before stage 1

of  $500\text{ cm}^3$  with a section of 40/30; the refrigerator return with a section of 40/30, the minimum length of the refrigerator is 400 mm; extraction sleeve made of filter paper with a diameter of 30 mm and a length of 90 mm, which is located in a mesh frame. The essence of the method is a single extraction of humic acids from an analytical sample of brown coal after removal of toluene extract with 1 % sodium hydroxide solution under heating, precipitation of humic acids with excess hydrochloric acid and determination of residual mass. When performing research, the yield of products was calculated, as well as the indicators of their proximate and ultimate analysis were determined.

## III. EXPERIMENT METHODOLOGY

Hybrid biopolymer nanocomposite materials and films were obtained by extruding pre-prepared raw materials in a single-screw laboratory extruder at a temperature of  $170\text{-}200^{\circ}\text{C}$  and a roll rotation speed of  $30\text{-}100\text{ rpm}$ . The L/D ratio of the extruder is 25, and to increase the uniformity of dispersed waste distribution in the finish compositions, 2 mass passes were used to obtain finished samples. It was made 20 parallel experiments for each composition, statistical processing was made by characteristics such as arithmetic mean, standard deviation and variation coefficient.

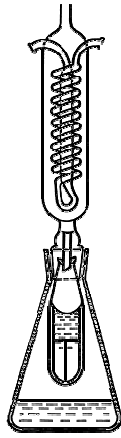


Fig. 1. Apparatus for determining toluene extract.

Dynamic light scattering (Zetasaizer NanoZS, Malvern) was used to measure the size of nanoparticles in the humic substances, aqueous dispersions of colloidal polyelectrolyte humic substances with concentrations from  $3 \cdot 10^{-4}$  to  $7 \cdot 10^{-5} \text{g} \cdot \text{mL}^{-1}$  for humic substances were prepared.

FTIR measurements were performed in transmission mode. For the transmission measurement, we used the FTIR microscope (IRscopeII) with liquid nitrogen cooled MCT detector, which is coupled to the FTIR spectrometer (BRUKER EQUINOX model 55 OPUS software).

The research of impact strength and breaking stress during bending of the samples was carried out on a pendulum head according to GOST 4647 and GOST 9550, respectively.

The concentration of metal ions in aqueous solutions was determined on a high-resolution PlasmaQuant PQ 9000 Elite optical emission spectrometer (Germany) with an inductively coupled plasma.

#### IV. RESULTS DISCUSSION

Table 3 shows the yield and quality of the studied samples. Analyzing the obtained data, we can conclude that the proposed methods allow obtaining humic substances and toluene extracts, which have very similar quality indicators, but the yield of these products varies. Option "0" allows obtaining from brown coal of Ukraine 14.86 % of toluene extract and 41.0 % of humic acids. Milder extraction conditions (option 1) resulted in a decrease in toluene extract yield from 14.86 % to 5.32 %. At the same time, the increase in the amount and concentration of NaOH led to an increase in the yield of humic acids from 41.0 % to 51.7 %.

TABLE II. YIELD AND QUALITY OF RESEARCHED SAMPLES

№	Sample	Yield, %	Proximate analysis, %		Ultimate analysis, %		
			$W^a$	$A^d$	$C^d$	$H^d$	$N^d + S^d + O^d$
0	Toluene extract	14.86	1.8	0.3	78.6	11.9	9.2
	Brown coal after toluene extraction	85.14	9.9	24.5	52.2	2.7	20.6
	Humic acids, $HA^{daf}_r$	41.00	11.2	3.9	57.4	3.8	34.9
	Brown coal after processing NaOH (1 %)	59.00 <sup>1</sup>	12.3	30.4	46.0	3.3	20.3

1	Toluene extract	5.32	2.0	0.1	79.6	12.4	7.9
	Brown coal after toluene extraction	94.68	10.4	22.1	54.8	3.6	19.5
	Humic acids, $HA^{daf}_r$	51.70	17.3	5.3	51.8	4.5	38.4
2	Brown coal after processing NaOH (2 %)	48.30 <sup>2</sup>	11.0	46.3	36.1	3.4	14.2
	Humic acids, $HA^{daf}_r$	48.32	14.2	5.1	61.7	4.0	29.2
	Brown coal after processing NaOH (2 %)	51.68	11.8	41.3	42.9	4.0	11.8
3	Toluene extract	1.790	1.7	0.3	79.6	12.6	7.5
	Brown coal after toluene extraction	98.21 <sup>3</sup>	13.5	42.0	45.5	4.2	8.3
	Humic acids, $HA^{daf}_r$	47.39	14.1	5.0	61.8	4.1	29.1
	Brown coal after processing NaOH (2 %)	52.61	11.6	41.0	43.0	4.0	12.0
3	Toluene extract	5.28	1.8	0.3	79.9	12.9	6.9
	Brown coal after toluene extraction	94.72 <sup>4</sup>	13.4	42.3	45.7	4.3	7.7
	Obtained toluene extract from humic acids	0.48	Not determined				

<sup>a</sup>  $W^a$  – moisture contents, %;  $A^d$  – ash content, %;  $S^d$  – the content of sulfur, %;  $C^d$  – the content of carbon, %;  $H^d$  – content of hydrogen, %;  $N^d$  – the content of nitrogen, %;  $O^d$  – content of oxygen, %.

<sup>1</sup> when calculating the yield of samples 0.3 and 0.4 yields of sample 0.2. accepted for 100 %

<sup>2</sup> when calculating the yield of samples 1.3 and 1.4 yields of sample 1.2. accepted for 100 %

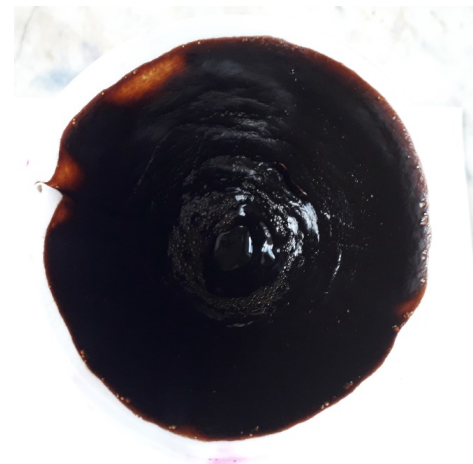
<sup>3</sup> when calculating the yield of samples 2.3 and 2.4 yields of sample 2.2. accepted for 100 %

<sup>4</sup> when calculating the yield of samples 3.3 and 3.4 yields of sample 3.2. accepted for 100 %

Determination of the yield of free humic acids to determine the yield of toluene extract from brown coal (var. 2 and 3) leads to the following. The yield of free humic acids is 47.39–48.32 % and the yield of toluene extract is 1.79–5.28 %, and the use of the extraction apparatus significantly (almost 3 times) increases the yield of toluene extract. In option 3, the yield of toluene extract from humic acids was further determined. It was found that it is possible to further remove 0.48 % of toluene extract from humic acids.

In Fig. 2 shows photos of precipitated humic substances on a paper filter in toluene extract.

Next, research was performed to determine the size of nano dispersed particles of humic substances by DLS. Since the particle size in the dispersed system depends on the concentration [1], the research was performed with solutions of different concentrations - Table. III.



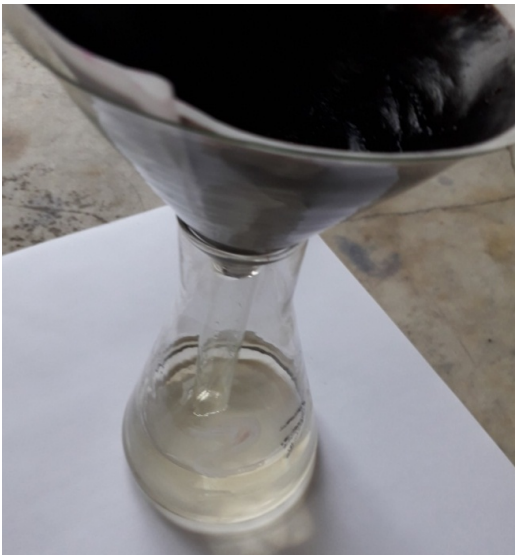


Fig. 2. Precipitated humic substances on a paper filter.

TABLE III. CHARACTERISTICS OF NANOPARTICLES OF HUMIC SUBSTANCES IN POLYELECTROLYTE DISPERSIONS

Sample of humic substances	C, g/mL <sup>-1</sup>	Size ± SD, nm	PDI ± SD
0	$3.4 \times 10^{-4}$	$342 \pm 200$	$0.40 \pm 0.02$
	$6.3 \times 10^{-5}$	$290 \pm 107$	$0.39 \pm 0.08$
1	$3.5 \times 10^{-4}$	$270 \pm 22$	$0.93 \pm 0.07$
	$3.6 \times 10^{-5}$	$52 \pm 2$	$1.00 \pm 0.04$
2	$3.6 \times 10^{-4}$	$368 \pm 240$	$0.41 \pm 0.02$
	$6.4 \times 10^{-5}$	$310 \pm 120$	$0.39 \pm 0.08$
3	$3.5 \times 10^{-4}$	$380 \pm 25$	$0.94 \pm 0.07$
	$3.6 \times 10^{-5}$	$60 \pm 9$	$1.00 \pm 0.01$

Based on the analysis, it was found that for nano dispersed particles of obtained humic substances from brown coal by four different methods the size is from 52 nm to 380 nm.

The size distribution in the submicron region in solutions of all humic substances is unimodally wide and, therefore, polydisperse based on the value of PDI: the values of the polydispersity index range from 0.38 to 1.00 and depend on the conditions of extraction of humic substances and their concentration. When diluting solutions of nano dispersed particles of humic substances, a decrease in particle diameter is observed, which may be associated with an increase in the thickness of the electric double layer as a result of a decrease in the concentration of counterions in the diffusion layer.

The research was performed which the method of IR analysis to determine the most characteristic functional groups in humic acids which were obtained from brown coal - table 4.

TABLE IV. IR SPECTRAL CHARACTERISTICS OF HUMIC SUBSTANCES

Wavenumber range (cm <sup>-1</sup> )	Functional groups
3380–340	phenolic –OH hydroxyl groups
2920–2940	aliphatic bands C – H
1650–1660	fluctuation vC=O
1540–1580	asymmetric vCOO– carboxyl
1380–1400	symmetric vCOO– carboxyl
1100	vCO (phenolic), vOH (aliphatic)
1040	vC–N
1005	vCO
910	out-of-phase δCH (aromatic)

Among the most characteristic spectral bands of humic acids should be noted: phenolic –OH hydroxyl groups at 3380–3400 cm<sup>-1</sup>, aliphatic bands C – H at 2920–2940 cm<sup>-1</sup>, symmetric vCOO– carboxyl and vCO (phenolic), vOH (aliphatic) at 1100 cm<sup>-1</sup>. It was found that the presence of these functional groups determines the ability of humic substances to act as a hybrid modifier of polylactide: conformational changes in its secondary structure and dipole-dipole interaction in the form of a hydrogen bond. Due to the increase in the degree of crystallization and the emergence of intermolecular and ester bonds in the formation of a more rigid network structure in the polylactide- humic substances system there is an increase in mechanical properties of hybrid biopolymer nanocomposite materials, which are shown in table 5.

TABLE V. MECHANICAL PROPERTIES OF HYBRID BIOPOLYMER NANOCOMPOSITE MATERIALS

Humic substances, % mass.	Impact strength, MPa	Breaking stress during bending, MPa
0	14	129
0.25	18.00	160.00
0.5	22.00	200.00
0.75	20.00	180.00

From the results shown in the table. 3 it is seen that the hybrid modification of polylactide with nano dispersed humic substances allows obtaining high-strength hybrid biopolymer nanocomposite materials, while the optimal content of nano dispersed humic substances in the polylactide- humic substances systems 0.5 % by mass.

The developed hybrid biopolymer nanocomposite materials based on polylactide and nano disperse humic substances were used as highly effective sorption membrane materials to reduce the content of heavy metal ions in oily natural, industrial and domestic waters and dosage forms for the production of drugs for the removal of heavy metal ions from the human body. These membrane hybrid biopolymer nanocomposite materials based on polylactide and nano disperse humic substances are porous polymer films with a pore size of 20 μm, and the working surface area of the membrane is  $28.26 \cdot 10^{-4}$  m<sup>2</sup>. In Fig. 3 shows the selectivity of membrane hybrid biopolymer nanocomposite materials based on polylactide and nano-dispersed humic substances. The research was conducted in a non-flow cell with a volume of 0.2 dm<sup>3</sup>, the surface area of the membrane was  $28.26 \times 10^{-4}$  m<sup>2</sup>, and the operative pressure was 0.2 MPA with the ambient temperature of 20–23°C. The solution for purification was mixed with a magnetic stirrer to reduce jellification at the rotation speed of 500 rpm.

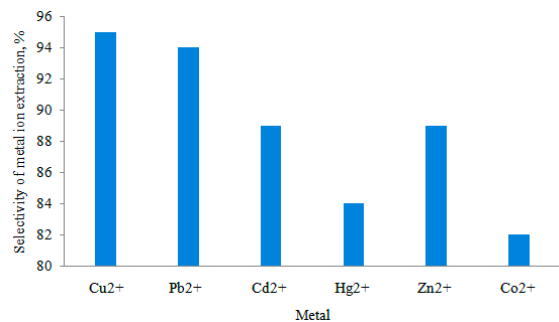


Fig. 3. Selectivity of metal ion extraction by membrane hybrid biopolymer nanocomposite materials based on polylactide and nano disperse humic substances.

Figure 3 shows that the obtained membrane hybrid biopolymer nanocomposite materials based on polylactide and nano dispersed humic substances have the maximum selectivity of extraction of metal ions in the ratio of  $\text{Cu}^{2+}$  – 95 % and  $\text{Pb}^{2+}$  – 94 %; and for metals such as  $\text{Cd}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Co}^{2+}$  it is from 82 % to 89 %.

Also based on the obtained hybrid biopolymer nanocomposite materials based on polylactide and nano disperse humic substances it is proposed to produce membrane-covering materials for wounds, implants and medical devices (fixing rods, plates, pins, screws, sutures, etc.) and products for dermatological treatment (for example, materials for facial lipoatrophy and repair of damaged tissues).

## V. CONCLUSIONS

In this work, hybrid polymer nanocomposite materials based on biopolymer polylactide and humic substances have been developed and studied. The processes of extraction of humic substances from brown coal were studied by four different methods, it was found that for the extracted nano disperse particles of humic substances the size is from 52 nm to 380 nm. The size distribution in the submicron region in solutions of all humic substances is unimodally wide and, therefore, polydisperse, which it is based on the value of the index of poly dispersion, which ranges from 0.38 to 1.00. It was found that the presence of these functional groups determines the ability of humic substances to act as a hybrid modifier of polylactide: conformational changes in its secondary structure and dipole-dipole interaction in the form of a hydrogen bond. Due to the increase in the degree of crystallization and the emergence of intermolecular and ester bonds in the formation of a more rigid network structure in the polylactide- humic substances system there is an increase in mechanical properties of hybrid biopolymer nanocomposite materials. Designed hybrid biopolymer nanocomposite materials based on polylactide and nano disperse humic substances were used as highly effective sorption materials to reduce heavy metal ions in oil natural, industrial and domestic waters and dosage forms in the production of drugs for the removal of heavy metal ions from the human body.

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