Mechanochemical Solid-Phase Reactions of Humic Acids with Metal Ions

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Abstract—The mechanochemical solid-phase reactions of humic acid with Cu^{2+}, Ni^{2+}, and Cd^{2+} metal ions were studied. The analysis of the mineral composition of humic acids by atomic emission spectrometry showed an increase in the concentrations of Cu^{2+}, Ni^{2+}, and Cd^{2+} ions after mechanical treatment.

The ability of humic acids (HAs) to enter into different donor−acceptor interactions with mineral components is responsible for one of the most important ecological functions in the biosphere. The binding of metal ions occurs due to the presence of a significant quantity of carboxyl and hydroxyl groups as the predominant substituents in the aromatic ring [1−3]. As a result of this, the mobility of metal ions can decrease upon the formation of insoluble complexes with HAs or, on the contrary, the mobility can increase upon interactions with low-molecular-weight fractions. The predominance of aromatic fragments like pyrocatechol in the structure increases the fraction of chelate interactions and ensures the formation of soluble stable complexes. The occurrence of the interactions of the hydroxide forms of metals with the formation of chelate compounds and physical adsorption processes along with the exchange reactions of HAs with metal cations should not be excluded.

Chemical modification related to hydrolytic oxidation processes is used for the enrichment of HAs in oxygen-containing functional groups [4, 5]. The amount of phenol fragments in HAs is increased by a factor of 2−4 by the conversion of phenols into quinones in an alkaline medium or by grafted copolymerization with hydroquinone, pyrocatechol, or *p*-benzoquinone [6].

Along with the above methods, the concentration of functional groups in HAs and the adsorption capacity can be increased under an intense mechanical action on humin-containing substances in the presence of different reagents [7, 8]. In this case, the yield of HAs increases and their molecular weight decreases. Mechanochemical synthesis methods make it possible to introduce substances into supramolecular humin-containing systems for producing materials with the regulated rates of extraction of components in an aqueous medium and for changing their reactivity and biological activity [9, 10]. Despite the fact that the mechanochemical transformations of HAs from peat and coal have been studied for a long time, the binding of metal ions by HAs in the course of treatment remains a debatable problem.

The aim of this work was to study the cation composition of metals in the mechanocomposites obtained upon the interaction of HAs with metal salts as a result of mechanochemical solid-phase reactions.

The HAs of high-moor peat with a 10% degree of decomposition and an ash content of 5% were chosen as test materials.

Humic acids were obtained from the peat by extraction with a 0.1 N solution of NaOH and precipitation upon the addition of hydrochloric acid to pH 2. The precipitate was filtered off, washed with distilled water to pH 7, and dried in a vacuum oven.

The solid-phase mechanical activation (MA) of HAs was carried out the following conditions: MA without a reagent and MA in the presence of 3 wt % of the heavy metal salts $CuSO_4 \cdot 5H_2O$, $NiSO_4 \cdot 7H_2O$, and $3CdSO_4 \cdot 8H_2O$ (analytical grade). The rotation frequency of drums was 1820 rpm, and the centrifugal acceleration was 600 m/s^2. The grinding bodies were steel balls with a diameter of 8−10 mm. The weight of balls in the load of a drum was 0.2−5 kg; the sample weight was 15−20 g, and the treatment time was 2 min.

The mechanocomposites obtained in the processes of the solid-phase mechanoactivation of HAs with the metal salts were dissolved in a 0.1 N solution of NaOH. In this case, alkali-soluble substances and a

dark brown precipitate were obtained. The precipitate was separated by centrifugation, washed with distilled water, and dried to constant weight. Hydrochloric acid was added to the alkaline solution to pH 2, and humic acids were separated.

The IR spectra of HAs were measured on a Nicolet-5700 Fourier transform IR spectrometer in KBr pellets at a ratio of 1 : 300.

The concentration of ionogenic acid groups was determined by potentiometric titration. In the titration of HAs, the ionic strength of solution was supported at a certain level with a saturated solution of sodium chloride [8]. In the titration curves obtained, three clear bends were detected in the ranges of pH 10−11 (phenol hydroxyls), pH 6.5−9.5 (carboxyl groups at the aromatic ring), and pH 2.5−6.5 (carboxyl groups at hydrocarbon chains). The equivalent points were calculated with the aid of numerical interpolation.

The distribution of carbon atoms in the structure of HAs was analyzed by ^{13}C NMR spectroscopy. The spectra were measured on a Bruker microwave spectrometer (Germany) with a carbon operating frequency of 125 MHz with the use of a Fourier transform procedure with accumulation. The accumulation time was varied from several hours to a few days. The test samples of HAs were dissolved in a 0.5 N solution of deuterated alkali. To exclude the nuclear Overhauser effect, the ^{13}C NMR spectra were recorded with the suppression of protons in the INVGATE mode. Tetramethylsilane was used as an external standard. The spectra were measured with a delay of 4 s between the pulses.

The quantitative determination of mineral components in HAs isolated from the peat and HAs isolated from the alkaline extract of a mechanocomposite was performed[1] by atomic emission spectrometry (AES) with MAES[2] The test samples of 0.0500−0.1000 g were placed in preliminarily calcined and weighed quartz crucibles; 20 μL of H_2SO_4 (conc.) was added, and the contents were ashed in a muffle furnace to constant ash weight with a gradual increase in the temperature to 450−500°C. The cooled crucibles were weighed; high-purity graphite powder (OSCh-6−4) was added to the mineral residue to reach the weight of the initial sample, and the mixture was homogenized. Analogously, a blank experiment was carried out without the addition of a test sample. The weighed portions of the analyzed, blank, and standard reference samples of a SOG-37 (GSO 8487-2013) graphite collector of

[1] Accredited Tomsk Regional Center of Collective Use of National Research Tomsk State University (accreditation certificate no. ROSS RU.0001.22NN07).
[2] Grand instrument complex, NPO Optical Electronics, Russia.

Table 1. Characteristics of the substances precipitated on the dissolution of mechanocomposites in a 0.1 N solution of NaOH

Sample	Precipitate content	Ash content of the precipitate
	wt %	
Untreated HAs	Not detected	4.2
MA + 3% $CuSO_4 \cdot 5H_2O$	6.7	36.9
MA + 3% $NiSO_4 \cdot 7H_2O$	10.3	52.1
MA + 3% $3CdSO_4 \cdot 8H_2O$	11.4	57.2

trace impurities of 0.015 g in weight were evaporated from the channel of a wineglass anodic electrode (depth and crater and neck diameters, 0.004, 0.0045, and 0.002 m, respectively). A tapered electrode (graphite electrodes of OSCh-7−4 grade were used) served as a cathode. Before the measurement of the spectra, 20 μL of a semi-alcohol solution of NaCl containing 5 wt % Na was introduced into the electrodes with the test samples and standard reference samples using a micropipette in order to stabilize conditions for the excitation of spectra.

The spectra were measured at the following parameters: direct current, 13 A; distance between the electrodes, 0.003 m; slot width, $3.0 \cdot 10^{-5}$ m; diaphragm, 0.005 m; number of accumulations, 160; accumulation time, 125 ms; and total exposure, 20 s.

Dark brown precipitates, which are insoluble in a 0.1 N solution of NaOH, were isolated from the mechanocomposites obtained upon the mechanical action on a mixture of HAs with the metal salts and their concentrations and ash contents were determined. Table 1 indicates that the smallest precipitate amount was formed from the HA +$CuSO_4$ mechanocomposite. The ash contents of HAs isolated from peat and the precipitates were 4.2 and 36.9−57.2 wt %, respectively. The precipitation of polyvalent metal hydroxides and the coagulation of HAs as a result of complexation with metal cations can be responsible for precipitate formation. The hydroxide content of the precipitate depends on the pH of solution. The precipitation of $Cu(OH)_2$, $Ni(OH)_2$, and $Cd(OH)_2$ occurs at pH 5.3−7.1, 7.7−9.5, and 8.2−9.7, respectively. In connection with this, the precipitates are different in terms of ash content.

The establishment of the mechanism of the mechanochemical solid-phase reactions of supramolecular systems is a complex problem. IR-spectroscopic data are indirect evidence for the formation of HA complexes with metal ions or metal hydroxides, which form precipitates. Humic acids have the same characteristic set of absorption bands (see the figure).

Transmittance
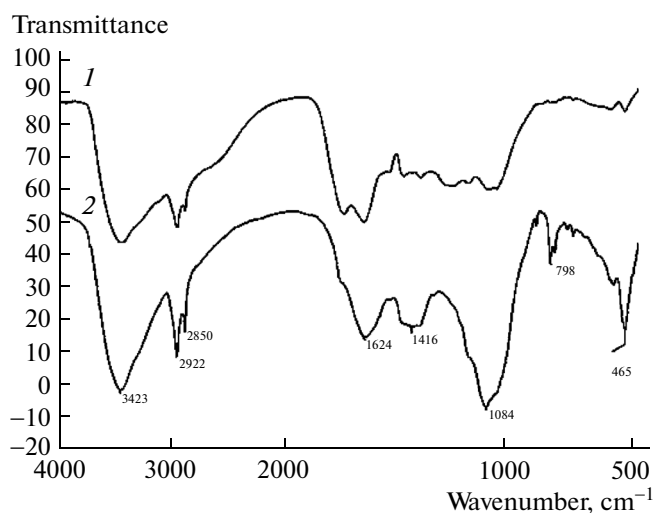
IR spectra: (*1*) initial HAs, (*2*) HAs separated from a mechanocomposite of HAs + CdSO$_4$, which is insoluble in NaOH.

The main maximum was detected in a range of 3399–3430 cm^{-1}, which characterizes the stretching vibrations of hydroxyl groups. An increase in the intensity of this absorption band for a precipitated complex is due to a redistribution of hydration water into the shells of functional groups. Absorption bands at 2922 and 2850 cm^{-1} characterize the stretching vibrations of C−H bonds in the aliphatic fragments of HAs. The frequencies of 1720 cm^{-1} were detected in the spectra to indicate the stretching vibrations of C=O bonds in undissociated carboxyl groups. The spectra contain bands due to the symmetrical (1400 and 1404 cm^{-1}) and asymmetric (1634 and 1630 cm^{-1}) stretching vibrations of carboxylate ions. These latter can be related to the vibrations of C−H bonds in the aromatic fragments of HAs. The bands at 1238, 1252, and 1254 cm^{-1} characterize the vibrations of C−O bonds and the deformation fluctuations of O−H in undissociated carboxyl groups.

The following differences in the spectra (see the figure) can be considered as evidence for the formation of HA complexes with the hydroxides of polyvalent metals, which are precipitated: A considerable decrease in the intensity of an absorption band at

1720 cm^{-1} with respect to that at 1624 cm^{-1} is indicative of the possible binding of the carboxyl group; obviously, an increase in the intensity of an absorption band at 1084 cm^{-1} is explained by the presence of a metal hydroxide species in the precipitate, whereas the appearance of bands in a range of 700–400 cm^{-1} results from the formation of M−O bonds.

The next stage of this work was a study of the composition of HAs soluble in 0.1 N NaOH. Table 2 summarizes the results of the potentiometric titration of ionogenic acid groups. The mechanochemical transformations of HAs with the salts of metals are accompanied by a decrease in the concentration of carboxyl groups at the aromatic ring, which suggests the formation of complexes with metal ions, depending on the nature of the ion. Changes in the functional composition of the samples obtained upon the interaction of HAs with CuSO$_4$ · 5H$_2$O and NiSO$_4$ · 7H$_2$O are similar; this fact is indicative of the occurrence of identical mechanochemical transformations.

A substantial increase in the amount of Ar−OH groups in the composition of solutes after the mechanoactivation of HAs with 3CdSO$_4$ · 8H$_2$O can be related to the presence of a hydrated ion, as it was earlier confirmed by the results of IR spectroscopy. Complex compounds are characterized by a low degree of their dissociation in aqueous solutions.

According to the results of ^{13}C NMR spectroscopy, the fragment composition of HAs undergoes changes after their mechanical activation with the solid metal salts (Table 3). The main difference between their composition in HAs before treatment and after mechanical activation is related to a decrease in the concentration of carbon atoms in functional (carboxyl and carbonyl) groups, which is most noticeable in the case of MA + 3% CuSO$_4$ · 5H$_2$O. In this case, the fraction of carbon in aromatic fragments increases.

The concentrations of mineral components in the samples of HAs isolated from the peat and from the alkaline solution of HA mechanocomposites with the metal salts were determined by AES (Table 4). It is well known that HAs, which are highly reactive, can occur in the form complex compounds with iron and aluminum, and a portion of them forms calcium and magnesium humates; however, free HAs also occur. Sili-

Table 2. Concentrations of functional groups in the composition of soluble humates

Mechanoactivation conditions	Concentration, mg-equiv/g		
	Ar−OH	Ar−COOH	Alk−COOH
Without MA	7.2	6.2	0.7
MA + 3% CuSO$_4$ · 5H$_2$O	8.0	4.2	1.6
MA + 3% NiSO$_4$ · 7H$_2$O	8.8	4.0	2.8
MA + 3% 3CdSO$_4$ · 8H$_2$O	13.2	2.4	Not detected

Table 3. Distribution of carbon in the structure of soluble humates according to the ^{13}C NMR spectroscopic data

Mechanoactivation conditions	Concentration of carbon atoms, rel %			
	COOH–	C_{Ar}, C_{Ar-O}	C_{Alk-O}	C_{Alk}
Without MA	17.3	34.1	24.0	24.6
MA + 3% $CuSO_4 \cdot 5H_2O$	12.4	38.1	23.8	25.6
MA + 3% $NiSO_4 \cdot 7H_2O$	14.6	39.1	24.8	21.5
MA + 3% $3CdSO_4 \cdot 8H_2O$	14.3	44.9	17.3	23.4

Table 4. Concentrations of mineral elements in the untreated HA sample and HAs isolated from the alkaline solution after mechanoactivation with the metal salts

Element	Concentration, wt % $\times 10^{-3}$			
	HAs	HAs+$CdSO_4$	HAs+$CuSO_4$	HAs+$NiSO_4$
Al	150	73	71	69
B	0.1	8.7	11	8.0
Ca	6.4	2.9	30	22
Cd	Not detected	45	Not detected	Not detected
Cu	»	Not detected	200	»
Fe	100	14	50	44
K	200	36	6.5	11
Mg	12	5.2	6.6	6.5
Mn	0.5	2	2	2
Ni	Not detected	Not detected	Not detected	48
P	74	54	110	130
Si	800	170	300	240
Zn	19	4	13	12

con, potassium, aluminum, iron, and phosphorus were detected in larger amounts in the untreated sample of HAs. Furthermore, the following elements occur in the composition of HAs: calcium, zinc, boron, magnesium, manganese, and titanium. Cadmium, copper, and nickel are absent from the structure of untreated HAs.

The analysis of the mineral composition of HAs isolated from the alkaline solution of a mechanocomposite of HAs with $CdSO_4$ showed the presence of cadmium in their composition in a concentration of 0.045 wt % (Table 4). In this case, the concentrations of aluminum, calcium, iron, silicon, phosphorus, and zinc considerably decreased, and the amount of boron and manganese increased; this can be explained by a redistribution of these elements between the precipitate and alkali-soluble HAs in the course of mechanoactivation.

The copper content of HAs isolated from the alkaline solution of a mechanocomposite of HAs with $CuSO_4$ was 0.2 wt % in the absence of copper from the initial sample (Table 4). The concentrations of iron, potassium, aluminum, and silicon noticeably decreased, but the amount of boron, calcium, manganese, and phosphorus increased. Changes in the concentration of other elements were insignificant.

The HAs isolated from the mechanocomposite of HAs with $NiSO_4$ contained nickel in a concentration of 0.048 wt % with its absence from the initial sample. A decrease in the amounts of aluminum, iron, potassium, and silicon and an increase in the mineral elements boron, manganese, calcium, and phosphorus were observed.

Analyzing the experimental results, we can draw a conclusion on the occurrence of mechanochemical solid-phase reactions between HAs and the metal salts $CuSO_4 \cdot 5H_2O$, $NiSO_4 \cdot 7H_2O$, and $3CdSO_4 \cdot 8H_2O$. This is evidenced by a decrease in the amount of carboxyl groups in the structure of HAs, which was confirmed by the IR-spectroscopic data, and the determinations of functional groups and the distribution of carbon atoms in the fragment composition of HAs. The concentrations of copper, cadmium, and nickel ions in the structure of mechanoactivated HAs were determined by AES in the absence of these ions from the initial sample. In this case, changes in the amounts of the other elements in the composition of HAs were noted; obviously, this is due to a redistribution of these ele-

ments between two HA fractions upon mechanoacti-
vation.

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